STUDIES ON THE INTERACTION OF CHROMIUM(III) WITH AMINO ACIDS

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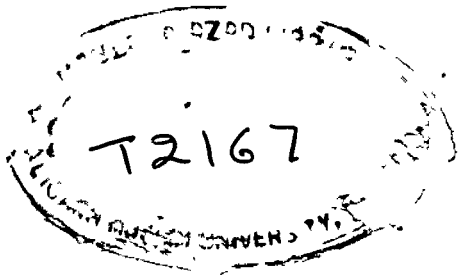

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ABSTRACT

There is exciting growth of the subject of the kinetics and mechanism of inorganic reactions with special reference to ligand substitution processes. Previously, only slow reactions could be studied by usual methods of kinetics but now this limitation has been removed by the development of fast reaction techniques. The substitution reactions of chromium(III) complexes have been the subject of interest from early history of coordination chemistry and still continue to be of such importance. The studies discussed in this thesis deal with the reaction which is defined as the replacement of coordinated water molecule from the aqua-complex by anion or neutral molecule of hexaaquochromium(III) with various amino acids (glycine, DL-∝-alanine, DL-valine, DL-serine, DL-methionine and DL-aspartic acid). The kinetic studies were carried out under pseudo-first-order conditions where ligand was in excess in comparision to metal ion concentration. Effects of ligand concentration, hydrogen ion concentration, temperature and ionic strength were studied. The mechanism consistent with the observed data is represented below.

The results can be divided in two classes: (1) monoamino, monocarboxylic acid (2) monoamino, dicarboxylic acid.

Mechanism of Anation of $Cr(H_2O)_6^{3+}$ with Monoamino, Monocarboxylic Acids:

The general reaction scheme for the anation of hexaaquochromium(III) with various monoamino, monocarboxylic acids which is found to be consistent with an associative interchange (I_a) type is interpreted by a stepwise mechanism in which ion-pair formation precedes the inner-sphere complex formation (the so-called 'Eigen Mechanism'):

$$H_2L^+ \underset{}{\overset{K_a}{\rightleftharpoons}} HL + H^+ \qquad (1)$$

$$(H_2O)_6Cr^{3+} + LH \overset{K_{ip}}{\rightleftharpoons} (H_2O)_6Cr^{3+},LH \qquad (2)$$

$$(H_2O)_6Cr^{3+},LH \xrightarrow{k_{an}} (H_2O)_5CrL^{2+} + H_2O \qquad (3)$$

$$Cr(H_2O)_5L^{2+} \xrightarrow[fast]{ligand} \text{Higher complexes}$$

(where HL represents zwitterion form of the amino acid).

The rate equation derived on the basis of the above mechanism is:

$$k_{obs} = \frac{d \ln [Complex]}{dt} \qquad (4)$$

$$= \frac{k_{an} K_{ip} K_a [Amino\ acid]_T}{[H^+] + K_a + K_{ip} K_a [Amino\ acid]_T} \qquad (5)$$

where $[Amino\ acid]_T$ = total concentration of the added monoamino, monocarboxylic acid.

By rearranging equation (5) we get equation (6) :

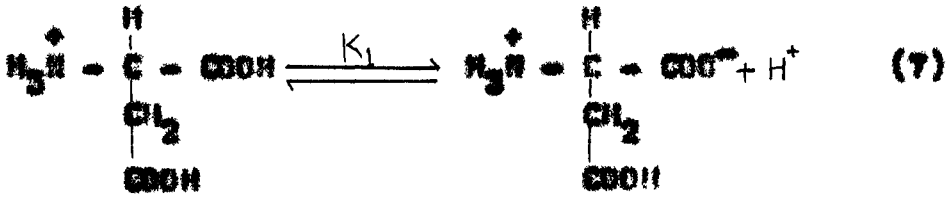
$$\frac{1}{k_{obs}} = \frac{1}{k_{an}} + \frac{[H^+] + K_a}{k_{an} K_{ip} K_a [\text{Amino acid}]_T} \qquad (6)$$

The above mechanism was supported by the plots of k_{obs}^{-1} vs. $[\text{Amino acid}]_T^{-1}$ which result in straight lines with intercepts independent of $[H^+]$.

The rate parameters used in equation (5) and their activation parameters were evaluated.

Mechanism of anation of $Cr(H_2O)_6^{3+}$ with Monoamino, Dicarboxylic Acid:

The mechanism for the anation of hexaquochromium (III) with aspartic acid (a monoamino, dicarboxylic acid) is different from that of the other amino acids (monoamino, monocarboxylic). The dependance of pseudo-first-order rate constant (k_{obs}) on hydrogen ion and aspartic acid concentrations is consistent with the following mechanism:



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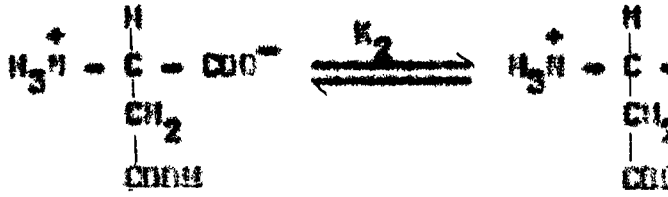

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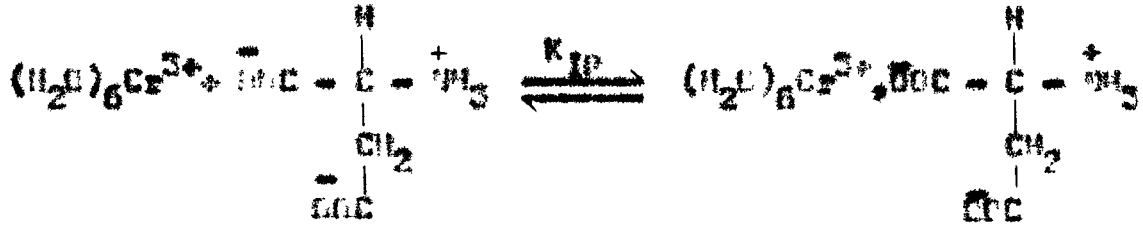

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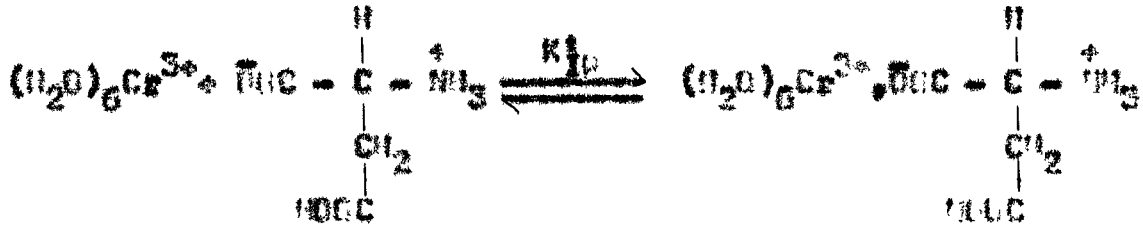

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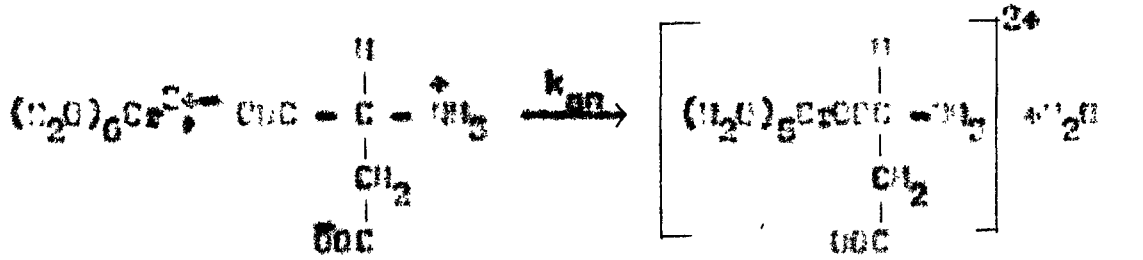

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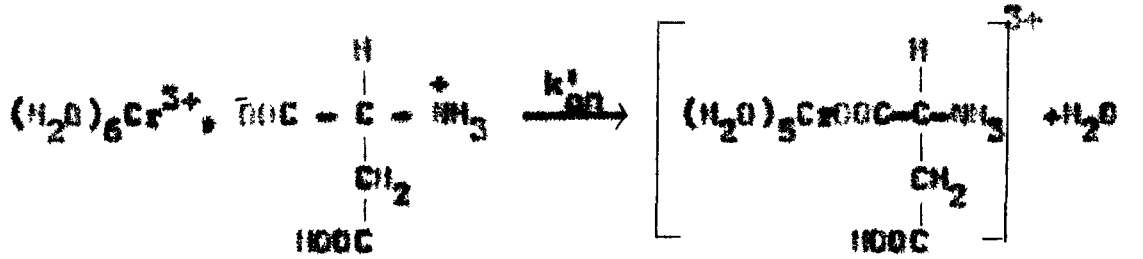

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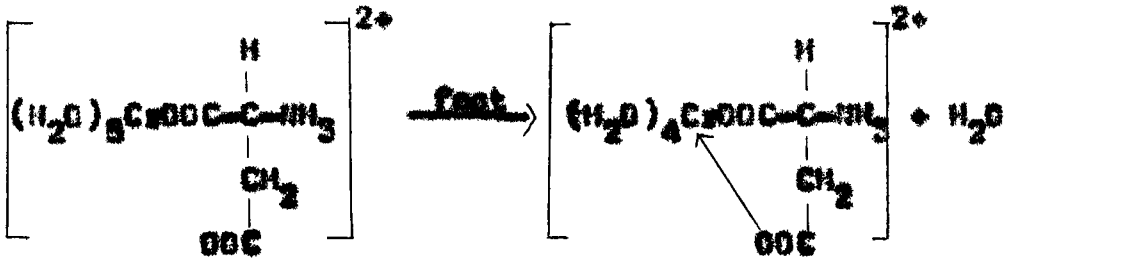

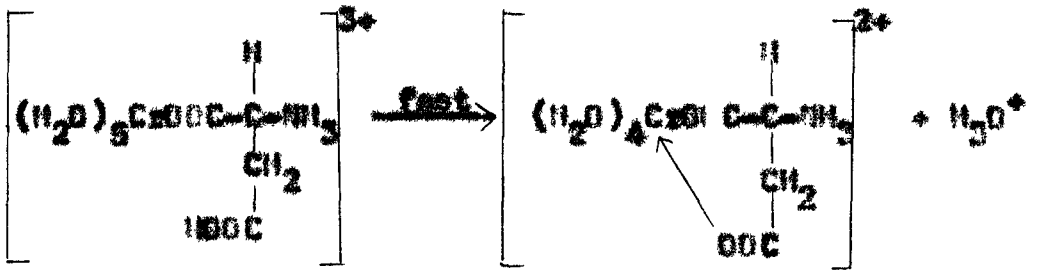

The rate equation derived on the basis of above mechanism is:

$$k_{obs} = \frac{d[\text{complex}]}{dt} = \frac{k_{an}K_{IP}K_2 + k'_{an}K'_{IP}[H^+][\text{aspartic acid}]_T}{[H^+]^2/K_1 + [H^+] + K_2\left[K_{IP}K_2 + K'_{IP}[H^+]\right][\text{Aspartic acid}]_T} \quad (13)$$

where $[\text{aspartic acid}]_T$ = total concentration of aspartic acid added. On rearrangement, equation (13) gives equation (14):

$$\frac{1}{k_{obs}} = \frac{K_{IP}K_2 + K'_{IP}[H^+]}{k_{an}K_{IP}K_2 + K'_{IP}k'_{an}[H^+]} \cdot \frac{[H^+]^2/K_1 + [H^+] + K_2}{k_{an}K_{IP}K_2 + k'_{an}K'_{IP}[H^+][\text{Aspartic acid}]_T} \quad (14)$$

The above mechanism was confirmed by plotting k_{obs}^{-1} vs. $[\text{Aspartic acid}]_T^{-1}$ at different concentrations of hydrogen ion. The plots were found to be linear for a given [hydrogen ion]. The intercepts of these lines were found to be dependent on $[H^+]$.

The values of rate parameters used in equation (13) were calculated and, from their values at different temperatures, activation parameters were calculated using Eyring equation.

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This is to certify that the work described in this thesis is the original work of Mr. Iqrar Ahmad Khan, done under my supervision. The thesis is suitable for submission for the award of Ph.D. degree in Chemistry.

(Kabir-ud-Din)

DEDICATED

TO

MY PARENTS

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I wish to express my feelings of gratitude and indebtedness to my supervisor, Dr. Kabir-ud-Din, who introduced me with the problem and its frontiers and guided me with keen interest throughout this endeavour. It was a real pleasure to work with him in an atmosphere of full freedom which he very generously provided me. Thanks are also due to Drs.M.A.Bag and A.A.Khan, Readers in the Department, for their help and affection.

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IQRAR AHMAD KHAN

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REVIEW ON THE COORDINATION CHEMISTRY OF CHROMIUM(III)

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REVIEW ON THE COORDINATION CHEMISTRY OF CHROMIUM(III)

Kinetic studies and stereochemical studies provide the most powerful method of investigating detailed reaction mechanisms. However, it is generally not possible to get absolute information. Thus, postulated mechanisms are essentially theories devised to explain the facts obtained by experiments. Like other theories, mechanisms are subject to change as new informations are uncovered, or, as new concepts are developed in related areas of science. Nevertheless, the postulation of reaction mechanisms is of greatest help in understanding and systematizing the study of an area of chemistry.

The area of chemistry in this case is that of coordination or complex compounds[1]. Such compounds contain a central atom or ion, usually a metal, and a cluster of ions or molecules surrounding it. It is characteristic of the complex that it retains its identity, more or less, even in solution, though partial dissociation may occur. The complex may be non-ionic or a cation or anion depending on the charges carried by the central atom or the coordinated groups. These groups are called ligands, and total number of attachments to the central atom is termed as the coordination number.

Transition metals which have got greater tendency to form the coordination complexes with various organic and inorganic ligands, are defined as those elements which have partly filled

d or f shells in any of their commonly occuring oxidation states. In view of this definition majority of all known elements are transition elements which can be subdivided into three main classes:

(a) Main transition or d-block elements

(b) Lanthanide elements and

(c) Actinide elements.

These transition elements have certain general common properties, and with a very few exceptions, they exhibit variable valence and their ions and compounds are usually coloured. The structure of the compounds of the transition metal ions could not be explained by ordinary theories of valency and therefore, Werner put forward the famous theory known as Werner's Coordination Theory, which has been a guiding principle in inorganic chemistry and in the theory of valence since its first publication.[2]

Following the studies of Werner and his contemporaries and the concept of the electron-pair bonding of Lewis and Sidgwick, the idea of the ligands was put forward which are defined as groups that can, in some way, donate electron-pairs to metal ions or other acceptors, thus forming the so-called coordinate bond. Pauling extended this approach further and developed the Valence Bond Theory of metal-ligand bonding. The theory was supplemented in fifties by Ligand Field Theory, which evolved out of a purely electrostatic theory known as Crystal Field

Theory, expounded by H. Bethe in 1929. According to this theory the interaction between metal ions and ligands is treated as purely electrostatic problem in which the ligands are represented as point charges. On the other hand, metal-ligand interaction can also be described in terms of molecular orbitals which are formed by the overlap of ligand and metal orbitals. It is not the main interest here to discuss the details of these theories, but, the concepts of acidity, basicity, isomerism and hydrolysis are also direct results of the coordination theory which has found increasing applications in many types of the chemical work e.g., the selection of organic precipitants for metallic ions, explanation of biological phenomenon, role of metal ions in leather tanning, dyeing of cloth and in regulating plant growth. Coordinating agents are used in winning metals from their ores, in electroplating, in catalysing reactions, in obviating the effects of undesirable catalysis, in precipitating metallic ions, in preventing their precipitation and in many other ways. Still other uses await study and exploration.

During the last thirty years the studies on the kinetics and mechanism of coordinated compounds started developing on the same lines as those of organic reactions. After going through the literature one can observe that this field is also well advanced although not yet at par with organic reaction mechanism. Both slow and fast reactions are being studied using different techniques but most of the work is still confined to those reactions which are relatively slow and can be investigated by

conventional methods. In this respect coordination chemistry of Co(III) and Cr(III) is quite interesting as their complexes played important part in the development of the coordination chemistry. Evidence accumulating over three decades has created a considerable degree of interest in the chemistry of chromium due to its biological activity and its nutritional role in plants, animals and man. At the same time, its long known use as mordant in dyeing, in tanning of leather, in electroplating, etc., makes it one of the most important transition elements. With this importance in view, the work on the coordination chemistry of chromium was undertaken. A brief review of the coordination chemistry of Cr(III) is given in the following pages with special reference to the work on the kinetics and mechanism which is our present field of interest.

COORDINATION CHEMISTRY OF CHROMIUM(III)

One of the most characteristic features of chemistry of chromium is the great ability of Cr(III) to form coordination compounds. In most aspects its complexes resemble with those of Co(III). The complexes of Cr(III) are inert and the rates of ligand interchange reactions of these complexes are usually slow. The complexes of Cr(III), however, are more susceptible to hydrolysis and formation of polynuclear complexes by olation than those of Co(III).

Types of the Chromium (III) Complexes

Chromium(III) forms a large number of complexes with different types of the ligands (organic and inorganic). Cr(III) complexes may be cations, anions or neutral molecules. Although the number of Cr(III)-complexes known is very large but they can be classified into small number of types. The different types of mononuclear Cr(III)-complexes with mono- and bidentate ligands are listed in Table 1. Some complexes of polydentate ligands are listed in Table 2. Chromium (III)- complexes have the ability to polymerise and numerous compounds are known that contain two or more chromium atoms per molecule linked by bridging groups such as -OH or other groups. Examples of such complexes are given in Table 3.

Stereoisomerism in Chromium(III) Complexes

The number of Cr(III)- complex is large not only because of the great number of ligands but also because of the numerous possibilities for isomerism. Isomeric forms of Cr(III)-complexes are illustrated by the three compounds of molecular formula

$Cr\,Cl_3 . 6H_2O$:

$[Cr(H_2O)_6].Cl_3$, $[Cr(H_2O)_5\,Cl]\,Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]\,Cl.2H_2O$

The water of crystallisation, 0-2 moles in the three compounds, is readily removed and easily distinguishable from the more strongly bound coordinated water molecules. Isomers of this

TABLE-1. Some mononuclear chromium(III) complexes of singly coordinating and bidentate chelating ligands

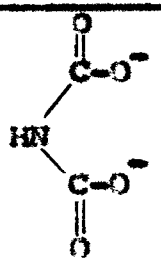
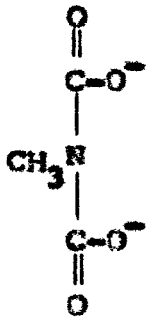
Type[a]	Ligands[b]
$[CrA_6]^{3+}$	A=H_2O; NH_3;NH_2CONH_2;½ en;½ pn;½ dipy;½ phen; ½ biguanide.
$[CrA_5B]^{3+}$	A,B= NH_3,H_2O
$[CrA_5X]^{2+}$	A,X= H_2O,Cl;H_2O;HO_3;NH_3,Cl;NH_3;Br;NH_3,NO_3;NH_3,NO_2.
$[CrA_3B_2X]^{2+}$	A,B,X= NH_3,H_2O,Cl; NH_3,H_2O,Br
$[CrA_4X_2]^{+}$	A,X= ½ en,ONO;½ en,Cl(cis); ½ en,SCN (trans);½ dipy, Cl; ½ phen,Cl; ½ dipy,½ ox; ½ phen, ½ ox
$[CrA_3BX_2]^{+}$	A,B,X= NH_3,H_2O, Cl; NH_3, H_2O, Br
$[CrA_3B_3]^{0}$	A,X= H_2O,Cl;C_2H_5OH,Cl;NH_3,Cl;T.P,Cl;Py,Cl; N-substituted amide, Cl
$[Cr(AX)_3]^{0}$	AX= acac;hfa;3-bromoacetylacetone;formylacetone; malonaldehyde,$CH_3COCH{=}(NHC_6H_4\ CH_3)CH_3$; dibenzoyl methane; alanine;glycine;methionine; diacetamide,dibenzamide
$[CrA_2X_4]^{-}$	A,X= NH_3,SCN;$C_2H_5NH_2$,SCN;py,SCN;H_2O,½ ox (cis); NH_3,½ ox(cis); ½ dipy,½ ox; ½ phen,½ ox
$[CrAX_5]^{2-}$	A,X= H_2O,Br
$[CrX_6]^{3-}$	X= CN,SCN; ½ ox

Type[a]	Ligands[b]

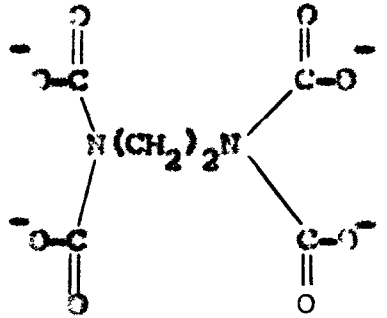
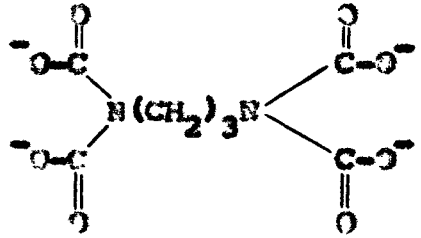
[a] A,D = singly coordinating neutral molecule or bidentate chelating neutral molecule; X = singly charged coordinated negative ion or bidentate doubly charged chelating ion; AA = bidentate chelating ligand coordinating via one neutral and one negative group.

[b] en = ethylenediamine; pn= propylenediamine; dipy =2,2'= dipyridyl; phen = 1,10-phenanthroline; py= pyridine; acac= acetylacetone; hfa=hexafluoroacetylacetone; THF = tetrahydrofuran; ox = oxalate

TABLE-2. Some Chromium (III) Complexes of polydentate ligands

Ligand	Formula	Type	Complexes
Iminodiacetate (IDA)		Tridentate	$[Cr(IDA)_2]^-$ (cis) $[Cr(IDA)(H_2O)_3]^+$
Methyliminodiacetate (MIDA)		Tridentate	$[Cr(MIDA)_2]^-$ (trans, facial) $[Cr(MIDA)(H_2O)_3]^+$
Triethylenetetramine (trien)	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	Tetrdentate	$[Crtrien\ Cl_2]^+$ (cis)

Conti.....

Ethylenediaminetetra-acetate (EDTA)		Pentadentate	$[Cr(EDTA)(H_2O)]^-$
Tetraethylenepentamine (tetren)	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	Pentadentate	$[Crtetren\ Cl]^{2+}$ $[Crtetren\ SCN]^{2+}$
1,3-Propanediaminetetra-acetate (PDTA)		Hexadentate	$[Cr(PDTA)]^-$

[a] Although EDTA is potentially hexadentate, it behaves as a pentadentate ligand here apparently because the last group is prevented from bonding because of strain in the rings which is removed by increase in ring size due to the additional $-CH_2-$ of PDTA.

TABLE-3. Some bridged chromium (III) Complexes

Compound	Bridging groups	Notes
$[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$	1 OH^-	"Rhodochromium(III)" ion
$[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$	1 OH^-	"Erythrochromium(III)" ion
$[(NH_3)_5CrOCr(NH_3)_5]^{4+}$	1 O^{2-}	"Basic rhodochromium(III)" ion
$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}$	1 OH^-	"Basic erythrochromium(III)"ion
$\|(NH_3)_5Cr(OH)Cr(NH_3)_4Cl\|^{4+}$	2 OH^-	"Chloroerythrochromium(III)"ion
$[(en_2Cr(OH)_2Cr\ en_2]Br_4 2.5H_2O$	2 OH^-	en= ethylenediamine, $NH_2CH_2CH_2NH_2$
$[(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2]^{4-}$	2 OH^-	-
$[(gly)_2Cr(OH)_2Cr(gly)_2]$	2 OH^-	gly= glycinate
$[(ala)_2Cr(OH)_2Cr(ala)_2]$	2 OH^-	ala= alaninate
$[(phe)_2Cr(OH)_2Cr(phe)_2]$	2 OH^-	phe= phenylalaninate
$[(phen)_2Cr(OH)_2Cr(phen)_2]^{4+}$	2 OH^-	phen= 1,10-phenonthroline

Conti .....

$\left[(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4\right]^{3+}$	1 OH^-, 1 SO_4^{2-}	-
$\left[Cr_2(\emptyset_2PO_2)_2(\emptyset_2PO_2)_2(H_2O)_4(OH)_2\right]$	2 $\emptyset_2PO_2^-$	Isomers: 4 meso; 4 inactive (centre of symmetry) 17 d,l pairs ($\emptyset = C_6H_5$)
$\left[Cr_3(OH)_2(HCOO)_6\right]HCOO$	6 $HCOO^-$	-
$\left[Cr_3(CH_3COO)_6O\right]^+$	6 CH_3COO^-	Cr atoms at corners of equilateral triangle. Oxygen atom at centre, 2-bridging acetate groups along each side.
$\left[Cr_4(OH)_6en_6\right].4\ H_2O$	6 OH^-	3 Cr atoms in triangular array with 1 in centre or 4 Cr atoms in tetrahedral structure (en= ethylene diamine)

type were called hydrate isomers by Werner, who recognised and described eleven types of isomerism of complex compounds.[4]

By far the most important types of isomers are the stereo-isomers, i.e., geometrical and optical isomers. Demonstration of correctness of Werner's views was in large part based on his prediction of stereoisomerism of metal complexes followed by preparation and separation of numbers and types of isomers predicted. Moreover, study of the mechanisms of reactions of metal complexes often involves consideration of the isomeric relations of reactants, intermediates and products.

The existence of stereoisomers of Cr(III)-complexes is possible because of the directed bonds of the Cr(III) structure. With coordination number six, Cr(III) has octahedral structure (Fig.1a) with Cr at the centre and the bonds directed towards the six vertices. For convenience, the convention showing only the horizontal plane 2,3,4,5 and the vertical axis 1,6 of the octahedron is used (Fig.1b); the six vertices are equivalent even though in the skeleton structure (b) two of them appear to differ from the other four. In counting the number of theoretically possible isomers, it must be remembered that bidentate ligands cannot span trans positions.

No stereoisomers are possible for the structures $[Cr\,A_6]^{3+}$, $[Cr\,X_6]^{3-}$, $[Cr\,A_5X]^{2+}$ and $[Cr\,AX_5]^{2-}$ since, interchanging the positions of the groups leaves the structure

unchanged. Geometrical isomerism arises with ions of the types $[CrA_4X_2]^+$ and $[CrA_2X_4]^-$ illustrated by cis - (1,2) - and trans-(1,6)-$[Cr(NH_3)_4Cl_2]^+$ (Fig.1 c,d). The chlorides of the cis - and trans-isomers are red-violet and green, respectively; the analogous Co(III) - complexes have the same colors as do the Cr(III) and Co(III)- complexes containing two moles of ethylenediamine or propylenediamine in place of the four moles of ammonia. Complexes of the type CrA_3X_3 also have two geometrically isomeric forms, i.e., cis-(1,2,3) and trans - (1,2,6) (Fig.1 e,f). Examples of such compounds are $[Cr py_3Cl_3]$, $[Cr(NH_3)_3Cl_3]$ and $[Cr(Nam)_3Cl_3]$ (py=pyridine; Nam = N-substituted amide). In the cis-form, three like groups are at the corners of a face of the octahedron; while in the trans-form three like groups lie in a plane at right angles to the plane of other three.

Since even the cis-isomers of complexes of types $[CrA_4X_2]^+$ and $[CrA_2X_4]^-$ have considerable symmetry, these complexes cannot have optical activity, which does arise, however, in the complexes containing two bidentate chelating ligands in place of the four singly coordinating molecules such as NH_3. This is illustrated by complexes such as $[Cr\ en_2\ Cl_2]^{3+}$ (Fig.1 g,h); the bracket represents the bidentate ligand. The trans form (g) has a high degree of symmetry while cis form (h) has no elements of symmetry. The latter, therefore,

has two forms which are related to each other as nonsuperposable mirror images, i.e., these two are optical isomers.

Although no isomers are possible with the types $[Cr\ A_6]^{3+}$ and $[Cr\ X_6]^{3-}$, their analogs with chelating ligands, $[Cr(\widehat{AA})_3]^{3+}$ and $[Cr(\widehat{XX})_3]^{3-}$, exist in d, l forms ($\widehat{AA}$ = bidentate symmetrical neutral chelating ligand such as ethylenediamine, $NH_2CH_2CH_2NH_2$; $\widehat{XX}$ = bidentate symmetrical negative chelating group such as oxalate, $C_2O_4^{2-}$). This is illustrated by the structure (i) of Fig.1. Chelates of the type $[Cr(\widehat{AX})_3]^0$ may also exist in d, l pairs ($\widehat{AX}$ = bidentate ligand such as 1,3-diketonate, or ion of a α- amino acid). The enantiomorphic forms are related to each other as three-bladed right- and left-handed propellers. Tartrate-type isomerism (d, l and meso) is possible with binuclear complexes (Fig.1 j,k). Chromium complexes of this type are

$[en_2Cr(OH)_2Cr\ en_2]^{4+}$ and $[(C_2O_4)_2Cr(OH)_2Cr\ (C_2O_4)]^{4-}$.

The number of possibilities increases when the ligand is unsymmetrical.

Complexes of type $[Cr(\widehat{AX})_3]$ have a structure like that of $[Cr(A_3X_3)]$ (Fig.1 e,f) except that each A is connected to an X. Thus, if AX is unsymmetrical, $[Cr(\widehat{AX})_3]$ will exist as a pair of geometrical isomers and each of these will be a d, l pairs, e.g., if AX is unsymmetrical 1,3-diketone such as trifluoroacetylacetone. Although acetylacetone (acac) has been classed

as a ligand of the $\widehat{AY}$ type (one neutral and one negative group bonding), no geometrical isomers of $Cr(acac)_3$ exist because resonance in the chelate rings makes it impossible to distinguish between the two oxygen atoms per ligand forming bonds to chromium.

A further increase in the possibilities of isomerism arises when a ligand is not only unsymmetrical but also asymmetric as exemplified by propylenediamine, $NH_2CH(CH_3)\ CH_2NH_2$ (pn). The complex $[Cr\ pn_3]^{3+}$ or <u>cis</u>-$[Cr\ pn_2\ X_2]^{+}$ (X = coordinated ion, such as Cl^-) may contain either the d or l form of the ligand; the complex ion may have either of the two configurations; and the unsymmetrical structure of the ligand leads to a structural isomerism superimposed on whatever geometrical isomerism is already present in the complex. For example three structural isomers of the complex <u>cis</u>-$[Cr\ pn_2Cl_2]^{+}$ are predicted because of the different possible relative positions of the methyl groups (Fig.1 l,m,n,); there would also be two isomers of the <u>trans</u>-form (Fig.1 o,p). The amino acids also belong to this class of ligands.

Polydentate ligands may also have different conformations.[5] For example, positions on C atoms of ethylenediamine-type ligands could have axial or equitorial orientation as indicated by a and e respectively of Fig.1q, e.g. the CH_3 groups of propylenediamine could be either axial or equitorial. In octahedral complexes, the latter is the preferred orientation because of steric interactions that would arise between axial groups and groups in octahedral coordination sites perpendicular to the chelate rings.

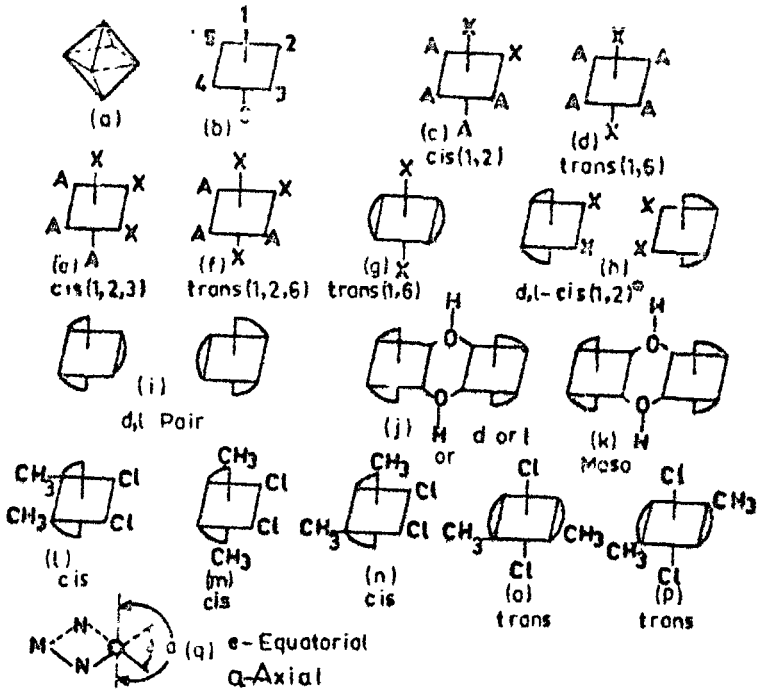


Fig. 1: Stereoisomerism of chromium (III) (a) Octahedral structure, coordination number 6. (b) Formal representation of octahedron; numbering system. (c,d) Geometrical isomers of $[Cr\,A_4\,X_2]^+$ (or $[Cr\,A_2\,X_4]^-$). (e,f) Geometrical isomers of $[Cr\,A_3\,X_3]$. (g,h) Geometrical and optical isomers of $[Cr\,\widehat{A}A_2\,X_2]^+$ (or $[Cr\,A_2\,\widehat{X}X_2]^-$)*. (i) Optical isomers of $[Cr\,\widehat{A}A_3]^{3+}$ (or $[Cr\,XX_3]^{3-}$). (j,k) Tartrate type isomerism possible for $[en_2\,M(OH)_2\,Men_2]^{4+}$ or $[(C_2O_4)_2\,M(OH)_2M(C_2O_4)_2]^{4-}$ (M=Co or Cr; en = ethylenediamine). (l,m,n) Structural isomers of cis-$[Cr\,pn_2\,Cl_2]^+$ (pn = propylene diamine). (o,p) Structural isomers of trans-$[Cr\,pn_2Cl_2]^+$. (q) Confirmations of coordinated pn and analogous ligands. •— = bidentate ligand.

SUBSTITUTION REACTI NS OF CHROMIUM (III)

The immediate environment of the central metal atom in a coordination compound is described by its coordination number and its coordination state and also by the geometry and relative positions of the ligands. The reaction of the coordination compounds may be related to the changes with the oxidation state, the changes in the coordination shell, or the changes in the coordinated ligands. The changes in the oxidation state or changes in the coordinated ligands have not been investigated systematically in the case of Cr(III) complexes and the bulk of the work is related with changes in the coordination shell. Chromium(III) ions in aqueous solution are always found coordinated with water molecules or with other coordinating species present in the solution. Therefore, the reactions related with the coordination shell are mainly those which are associated with the replacement of one ligand by another. Thus the discussion of the kinetics and mechanism of the reactions of Cr(III) complexes is mainly confined to the ligand substitution reactions. A detailed account of the studies related with the kinetics and mechanism of such reactions is, therefore, being given in the following pages.

Nature of Substitution Reactions

Substitution reactions include the replacement of one ligand by another in a complex, or one metal ion by another.

Following the terminology used by Hughes and Ingold in organic chemistry, we may call these as S_N and S_E reactions, respectively.[6] The terms refer to nucleophilic substitution and electrophilic substitution. In coordination chemistry the central atom is an electrophilic reagent and the ligands are nucleophilic reagents.

$$Y + M - X \longrightarrow M - Y + X \qquad S_N$$

$$M' + M - X \longrightarrow M' - X + M \qquad S_E$$

The nucleophilic substitution reaction is a special type of general acid-base reaction, in which the metal ion functions as a Lewis acid and the replacing ligand as a base. Two fundamentally different paths can be visualised for these reactions, S_N1 (substitution, nucleophilic, unimolecular) and S_N2 (substitution, nucleophilic, bimolecular).

An S_N1 reaction goes by a two step mechanism in which the first step is slow unimolecular hetrolytic dissociation and in the second step the rapid coordination of the incoming ligand to the metal ion occurs.

$$M - X \underset{\text{slow}}{\rightleftharpoons} M + X$$

$$M + Y \xrightarrow{\text{fast}} M - Y$$

The rate determining step is the rupture of metal-ligand bond.

An S_N2 reaction is one involving a bimolecular rate-determining step in which one nucleophilic reagent displaces another. This may be shown as:

$$Y + M - X \longrightarrow Y \cdots M \cdots X \longrightarrow Y - M + X$$

The rate-determining step is the partial formation of a new metal ligand bond plus weakening of another such bond.

Another possibility is the four centre mechanism,[7] in which two acid - base complexes simultaneously exchange groups.

$$M - X + M' - Y \longrightarrow \begin{matrix} & X & \\ M & & M' \\ & Y & \end{matrix} \longrightarrow M - Y + M' - X$$

This process does not require the expulsion of the group X or Y into the solution as free ions or molecules. This is possible for those cases in which the X or Y is very unstable as a free particle and the bond M - X or M - Y is very covalent so that the dissociation into the ions is difficult and the solvent is nonpolar or absent.

Classification of Ligand Substitution Mechanism

Langford and Gray[8] have referred to sequences of elementary steps which make up the reaction mechanism as stoichiometric mechanism and propose that the substitution mechanism may follow three pathways:

(a) Dissociative path (D) , in which the leaving ligand is lost in the first step, producing an intermediate of reduced coordination number

$$MX_n \underset{+X}{\overset{-X}{\rightleftharpoons}} MX_{n-1} \underset{-Y}{\overset{+Y}{\rightleftharpoons}} MX_{n-1}Y$$

(b) Associative path(A), in which the entering ligand adds in the first step, producing an intermediate of increased co-ordination number

$$MX_n \underset{-Y}{\overset{+Y}{\rightleftharpoons}} MX_nY \underset{+X}{\overset{-X}{\rightleftharpoons}} MX_{n-1}Y$$

(c) Concerted path or Interchange(I)

A reaction assigned an "interchange" mechanism merely reflects the fact that the experimental data do not provide solid evidence for the occurrence of an intermediate but it does not imply the non-existence of such an intermediate

$$MX_n \cdots Y \longrightarrow MX_{n-1}Y \cdots X$$

For a dissociative process, the entering group does not interact directly with the reaction centre in the transition state, whereas for the associative process such a reaction takes place. The experimental means of distinguishing the probable mechanism then becomes possible. In a dissociative

activated intimate mechanism the rate of reaction should be insensitive to the nature of the entering group except for small effects arising from "solvation" interaction while the rate of an associatively activated mechanism should be very sensitive to the nature of entering group. There are many kinetic and stereochemical techniques that can be used to detect the presence of reactive intermediates. Such tests provide means for assigning an A or D label which can only be done when the evidence for the approximate intermediate is forthcoming. The interchange mechanism presents a great problem, in the sense that its demonstration is negative, i.e. an I-mechanism is assigned when no evidence can be produced for a reactive intermediate. The interchange process can have either associative or dissociative activation and therefore I_a and I_d mechanisms are visualised. The identification of I_a mechanism is easy due to the synchronous bimolecular process but the I_d mechanism presents some problem. The D and I_d processes are best distinguished in terms of the life-time of the intermediate. If it lives long enough to equilibrate with its solution environment it will obey the test characteristic of a D mechanism. On the other hand if interacts with environment it has inherited then the mechanism is I_d.

Most of the studies on the kinetics and mechanism of octehedral complexes have been discussed in the light of these

four types (A, I_a, I_d and D) of mechanisms. Their characteristics are summarized in Table 4.

TABLE-4. Classification of ligand substitution mechanisms

Stoichiometric mechanism			
Mode of activation	Intermediate of increased coordination number	one step process	Intermediate of reduced coord. number
Associative activation	A	I_a	
Dissociative activation		I_d	D

Substitution reactions of Co(III) complexes which have been studied extensively may be classified in the following four important classes:

Acid hydrolysis

The most common reaction of a metal complex , and the one studied to the greatest extent, is the reaction between the complex and the solvent water. Acid hydrolysis reaction consists of displacement of a coordinated ligand by water in

acidic solution (aquation). Some acid hydrolysis rate constants for Cr (III) complexes are listed in Table-5 in comparision with the constants for hydrolysis of the analogous Co (III) complexes.[9,10]

TABLE-5. Acid hydrolysis rate constants[9]

	Cr(III)		Co(III)	
Complex	$K_{acid}(s^{-1})$	t(°C)	$K_{acid}(s^{-1})$	t(°C)
$[M(NH_3)_6]^{3+}$	2.5×10^{-5}	25	(very slow)	-
$[M(NH_3)_5H_2O]^{3+}$	1.0×10^{-6}	40	7.0×10^{-6}	25
$[M(NH_3)_5Cl]^{2+}$	1.0×10^{-5}	25	1.7×10^{-6}	25
$[M(NH_3)_5Br]^{2+}$	5.0×10^{-5}	25	6.3×10^{-6}	25
$[M(NH_3)_5I]^{2+}$	2.0×10^{-5}	0	1.0×10^{-5}	25
$[M(NH_3)_5NCS]^{2+}$	1.0×10^{-7}	25	3.0×10^{-9}	25
$[cis\text{-}Men_2Cl_2]^{+}$	3.3×10^{-4}	25	3.5×10^{-4}	25
$[trans\text{-}Men_2Cl_2]^{+}$	3.8×10^{-5}	25	3.9×10^{-5}	25
$[Cr(H_2O)_5\ NCS]^{2+}$[a]	9.1×10^{-5}	25	-	-

[a] Ref.10

In acid hydrolysis reactions, since the entering ligand, H_2O, is present at a concentration of about 55.5 M

and its concentration essentially remains constant, a first order rate law gives no indication of what the order is with respect to H_2O. Although the question cannot be answered definitely, a predominantly S_N1 mechanism is supported by some of the data. For example, the variation of the rate depending on the ligand Y follows the variation of thermodynamic stability of the complex ions, indicating that M - Y bond breaking is an important factor in producing the transition state. The order of decreasing lability of the ligand displaced is about the same as the order of the spectrochemical series (increasing ligand field stabilization); i.e.

$HCO_3^- > HO_3^- > I^- > Br^- > H_2O > Cl^- > SO_4^{=} > F^- > NH_3 > CH_3COO^- > NCS^- > NO_2^-$.[9,11]

Numerous investigators have studied the kinetics of aquation of complexes of the type $[Cr(H_2O)_5X]^{2+}$ (X= F, Cl, Br, I, H_2PO_2, N_3, NCS). A recent addition to the list is $[Cr(H_2O)_5SO_4]^+$, which is interesting because the ionic charge is one less than that of the others.[12] Several reaction pathways are available in aquation mechanisms, i.e. depending on $[H^+]$, $[H^+]^{-1}$ and $[H^+]^0$. A trend is discernible comparing the reaction parameters for the $[H^+]^{-1}$ pathway with those of the $[H^+]^0$ and $[H^+]$ pathways. As the order with respect to $[H^+]$ becomes more positive, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ become less

positive; the only exceptions are the parameters for the sulfato complex. It is concluded that $[H^+]$ pathway is important only for complexes containing somewhat basic ligands.

In an acid solution of $[Cr(H_2O)_5I]^{2+}$ containing Cl^- or Br^-, both aquation and anation occur.[13] Anation of the product of aquation $[Cr(H_2O)_6]^{3+}$ is excluded since this is known to be slow.[14] A possible mechanism involves competition by H_2O and X^- for a position on a 5- coordinate intermediate:

$$[Cr(H_2O)_5X]^{2+} \longrightarrow [Cr(H_2O)_5]^{3+} + I^-$$

$$[Cr(H_2O)_5]^{3+} + X^- \longrightarrow [Cr(H_2O)_5X]^{2+}$$

$$[Cr(H_2O)_5]^{3+} + H_2O \longrightarrow [Cr(H_2O)_6]^{3+}$$

Alternatively, the mechanism may involve the *trans* effect.[15] In the aquation of $[Cr(H_2O)_5I]^{2+}$ in aqueous $HClO_4$ containing H_2O^{18}, the product, $[Cr(H_2O)_6]^{3+}$, contains two labeled water molecules. One of these is the molecule that displaced the iodide ion; it was concluded that there was exchange of a coordinated water molecule prior to the aquation as a result of *trans* effect, i.e. labilising effect by the iodide ion on the *trans* position. Only slow H_2O exchange occurs with $[Cr(H_2O)_5Cl]^{2+}$.

Replacement of coordinated halide in the following complexes by H_2O occurs with essentially complete retention of

configuration[16] (1) cis-$[Cr(NH_3)_4H_2O\ Cl]^{2+}$; (2) trans-$[Cr(NH_3)_4Cl_2]^+$; (3) trans-$[Cr(NH_3)_4\ Br\ Cl]^+$; (4) trans-$[Cr(NH_3)_4H_2O\ Cl]^{2+}$. The first - order rate constants ($[H^+]$= 0.08 to 1.00 M) ranged from 1.13 to 2.00×10^{-4} s^{-1}. The order of increasing rate was: 4,1,2,3. The trends in reaction rates are the same as those reported for the analogous ethylenediamine[17-19] complexes.

Base hydrolysis

In base hydrolysis, a coordinated ligand is ultimately replaced by OH^-, although the process may not be direct. Some reaction rate constants (k_{OH^-}, $M^{-1}s^{-1}$) are[11]

cis-$[Cren_2Cl_2]^+$;[Cr(III)], 2.7×10^{-2}(25°);[Co(III)], 10^3(25°);

trans-$[Cren_2\ Cl_2]^+$; 3.7×10^{-2}(25°); 3×10^3 (25°). The rates for the Co(III) complexes are about 10^5 times those for the Cr(III) complexes.

It is apparent that the mechanism cannot be the same. It has been suggested that some Co(III) complexes of NH_3 and amines can react by the S_NICB mechanism (substitution, nucleophilic, unimolecular; conjugate base) in which the fast reaction is a combination of OH^- with a proton from, for example, NH_3, leaving a coordinated NH_2^-, followed by a slow (rate controlling) reaction with water converting the NH_2^- back to NH_3 and coordinating the resulting OH^-.

Exchange reactions[20,21]

The replacement of a ligand present in the inner coordination shell of the metal ion by the same type of the ligand present in the solution may be called an exchange reaction. Exchange of a ligand with the coordinated ligand can be followed by the use of isotopic tracers. The inert character of Cr(III) complexes is demonstrated by the low rate of exchange of H_2O^{18} with coordinated water of $Cr(H_2O)_6^{3+}$; the rate constant (at 27°) is 2 to 5 X 10^{-6} min^{-1}, depending on the concentration, and is constant over the range of $[H^+] = 10^{-2}$ to 1.5 M. The activation energy is about 24 kcal/mole. The question whether this reaction is S_N1 or S_N2 has not been answered; either type fits the rate law:

$$\text{rate} = k\left[Cr(H_2O)_6\right]^{3+}$$

In the study of exchange reactions with ligands other than water, aquation may cause complications. For example, the exchange of urea with $[Cr(NH_2CONH_2)_6]^{3+}$ is slow in water and cannot be followed readily because of rapid aquation although the exchange has been measured in methanol.

Anation reactions

The replacement of the coordinated water molecule from the aquo-complex by anion or neutral molecule is the reverse of an acid hydrolysis reaction and is called anation reaction.[22] This may be represented by the following equations:

$$M(H_2O)_n^{+m} + X^{-1} \longrightarrow M(H_2O)_{n-1}X^{+(m-1)} + H_2O$$

$$M(H_2O)_n^{+m} + X \longrightarrow M(H_2O)_{n-1}X^{+m} + H_2O$$

In general, the rate of reaction of an aquo-ion with a ligand is not strongly affected by the nature of the ligand and the rates for a given ion are about the same as the rates for water exchange for that ion. Presumably these facts are accounted for a reaction mechanism comprising of two steps: (1) formation of outer-sphere complex; (2) elimination of water from aquo ion.[23]

Such reactions have been studied in detail for Co(III), Rh(III) and Cr(III) complexes and their mechanisms have been proposed. The work done on the anation of Cr(III) complexes is reviewed here in detail.

Hamm and Davis[24] studied the formation of dioxalato-diaquo-chromium(III) ion from hexaaquochromium(III) and oxalate ion. The rates of reaction of the two species $\left[Cr(H_2O)_4(C_2O_4)\right]^+$ and $\left[Cr(H_2O)_2(C_2O_4)_2\right]^-$ were determined polarographically by measuring currents at diffusion plateaus. The reactions were found to be consecutive and first-order with respect to the reacting metal species. The rate of the first step was found inversely proportional and that of the second one was independent of the hydrogen ion concentration. Both the rates were independent of oxalate ion concentrations.

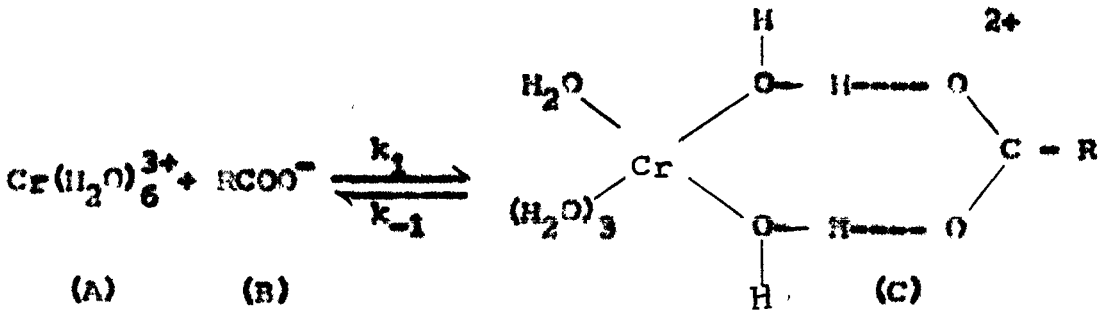
Hamm and Perkins[25] produced the evidence for the existence of malonato complexes of chromium (III) containing one, two and three malonate groups per chromium atom. The values of activation parameters were calculated and compared with those of oxalate with Cr(III). The comparision between malonate and oxalate for the first and second chelation steps indicated that the slow steps were nearly identical. Later Buchital and Taube[26] studied the monodentate form of the malonate-Cr(III) complex. They suggested that the substitution was as slow as it was for exchange of water, particularly because the local concentration of the free carboxalate ion was high and the displacement of water is not greatly assisted by the incoming carboxyl group. Banerjee and Chatterjee[27] studied the formation of tetraaquo-monomalonato-Cr(III) ion from hexaaquochromium (III) ion and malonic acid. A comparision of the values of the activation parameters, ΔH^* and ΔS^*, for this complex system with the corresponding literature values for the water exchange of $[Cr(H_2O)_6]^{3+}$ ion, suggests that in the present system the ion- pair reacts essentially by S_N1 process.

Kelm and Harris[28] reported the substitution reactions of oxalate complex ions. They studied the kinetics of the anation reaction of cis-bis-(oxalato)- diaquo chromium(III) ion with oxalate ion in aqueous solution. The observed first-order rate constant was described by equation:

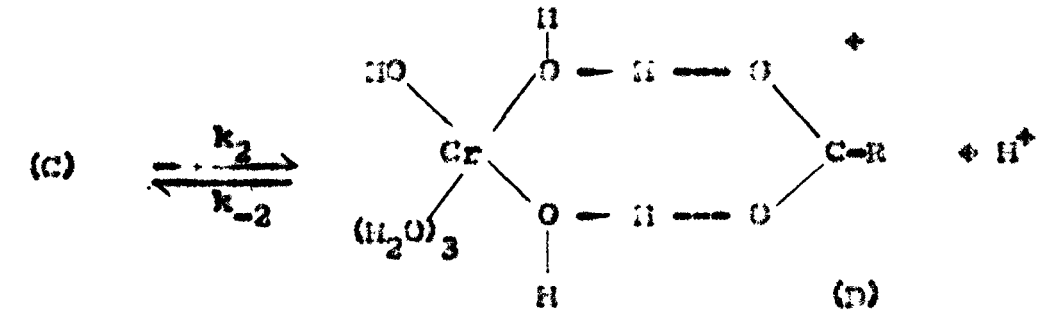
$$K_{obs} = \frac{k_w K_1 [HC_2O_4^-]}{1 + K_1 [HC_2O_4^-] + K_2 [C_2O_4^{2-}] / \{1+K_2[C_2O_4^{2-}]\}}$$

where K_1 and K_2 are association constants for bioxalate and oxalate respectively and k_w is the rate constant of water replacement. Banerjea and Chaudhuri[29] reported the kinetics and mechanism of formation of tetra-aquo-mono-oxalato-chromium(III) from hexaaquochromium (III) ion and oxalic acid in aqueous perchloric acid media. On the basis of the values of ΔH^* and ΔS^* they suggested that the dissociation of the first chromium (III) - H_2O was important in the transition state.

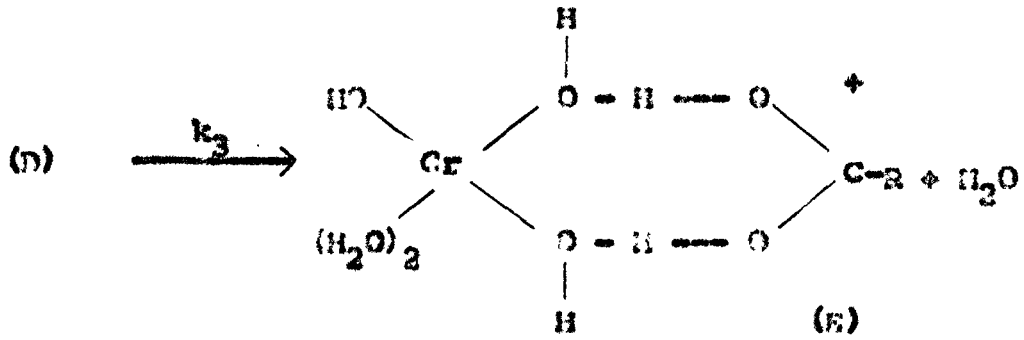
Hamm and coworkers[30] studied the rates of reactions for a series of organic acid anions (acetate, glycolate, lactate, phthalate, citrate and tartarate) with Cr(III) by polarographic method. From similarities in these rates and those previously reported for oxalate and malonate, following general mechanism was proposed, which involve the dissociation of the water molecule as the slow step:



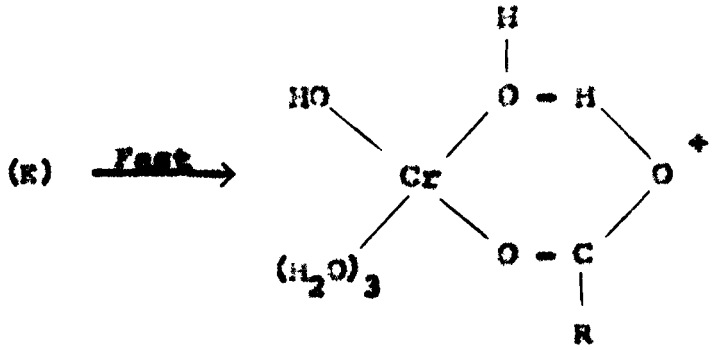
(A) (B) (C)



(C) (D)



(D) (E)



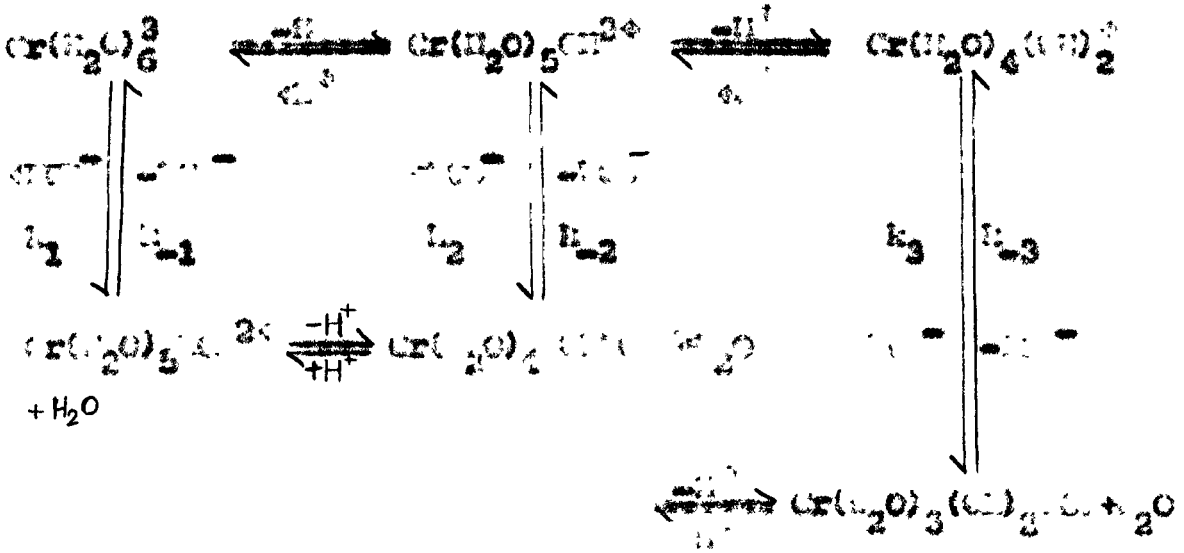
(E)

The rate equation consistent with the above mechanism is

$$d(Cr^{3+})/dt = k_3K_1K_2[Cr_t]/[H^+]([H^+] + K_2) \quad K_1[B]$$

where $[Cr_t]$ represents the concentration of the total polarographically measureable chromium.

Watmus and King[31] reported the equilibrium and kinetic studies of the interaction of chromium (III) with thiocyanate ion. They proposed the following mechanism:



The rate equations consistent with the above mechanism are:

$$d\left[Cr(H_2O)_5SCN^{2+}\right]/dt = \left[Cr(H_2O)_6^{3+}\right]\left[SCN^-\right]\left[\frac{k_2}{[H^+]} + \frac{k_3}{[H^+]^2} + k_1\right]$$

$$\frac{d[SCN^-]}{dt} = \left[Cr(H_2O)_5SCN^{2+}\right]\left[k_{-1} + \frac{k_2}{[H^+]} \quad \frac{k_{-3}}{[H^+]^2}\right]$$

Banerjea and Chaudhuri[32] studied the rate of formation of chromium (III) - glycine complexes by following the interaction of $\left[Cr(H_2O)_6\right]^{3+}$ and glycine spectrophotometrically in weakly acidic media. A comparison was made of the position of the two ligand field bands in the visible spectrum of this complex with those in a large number of other chromium (III) complexes of oxygen and nitrogen containing ligands. The following reaction mechanism was suggested:

$$GH \rightleftharpoons G^- + H^+$$

$$G^- + Cr(H_2O)_6^{3+} \xrightarrow[\text{slow}]{k} Cr(H_2O)_5G^{2+} + H_2O$$

$$Cr(H_2O)_5G^{2+} \xrightarrow{G^-} \text{Higher complexes}$$

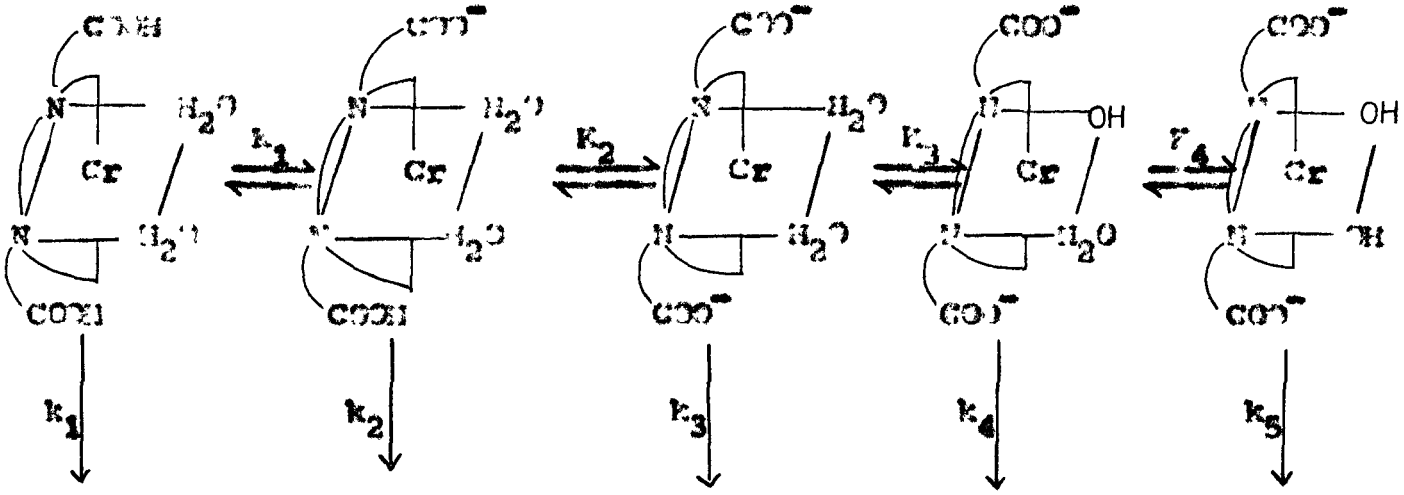
(bis and tris)

$$\text{Rate} = k'_{GH}\left[\frac{T_G - T_A}{[H^+]}\right][Cr^{3+}]$$

where K_{GH} = dissociation constant of glycine.

Deponson[33] reported the formation rates of mono-substituted-chromium(III) complexes in aqueous medium for Cl^-, Br^-, I^-, NO_3^-, SCN^- and NCS^-. He proposed a bimolecular mechanism and discussed about the proton ambiquity involved in the mechanism. Thusius[34] reported the formation of mono-substituted-chromium(III) complexes with Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, H_3PO_2, etc. He proposed an associative interchange (Ia) type mechanism and the temperature at which rates for all the reactions were same (iso-kinetic temperature) was 50°. Casey, Jones and Swaddle[35] studied the mechanism of substitution reactions of azido-pentaaquochromium (III) complexes at 25°. They proposed an associative interchange (Ia) type mechanism for acid-independent substitution processes in aquochromium(III)-complexes, but a conjugal base such as $Cr(H_2O)_4OHX^+$, appears to react by a dissociative interchange (I_d) mechanism.

Tomkley , Sykes and Gans[36] studied the kinetics of the interconversion of quadri-dentate and quinque-dentate chromium (III) - EDTA (aquo) complexes and they attempted to identify the sixi-dentate complex. The following mechanism was proposed:



The rate equation derived on the basis of above mechanism is

$$k_{obs} = \frac{k_1[H^+]^4 + k_2K_1[H^+]^3 + k_3K_1K_2[H^+]^2 + k_4K_1K_2K_3[H^+] + k_5K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

Banerjea and Sarkar[37] studied the kinetics of formation of acetatopentaammine chromium(III) ion from aquapentaammine chromium (III) complex in acetic acid - sodium acetate media.

The reaction was found to proceed by two concurrent paths, one of which was independent of [acetate ion] while the other was first order with respect to acetate ion concentration. The rate constants for both the steps and corresponding activation parameters

were evaluated. The results were consistent with an S_NI mechanism for the acetate independent path and an S_NI IP (Ion-pair) mechanism for the acetate dependent path. Evidence for the ion-pair formation was obtained.

Swaddle[38] reviewed many possibilities in the substitution reactions of octahedral complexes on the basis of activation parameters and linear free energy relationship.

Kelm and his coworkers[39,40] investigated in detail the mechanism of formation of oxalato complex of chromium(III) in aqueous medium. The rates of successive oxalate additions to $Cr(H_2O)_6^{3+}$ were found 4.0×10^{-5} l mole^{-1}s^{-1}, 5.3×10^{-4} l mole^{-1}s^{-1} and 1.4×10^{-4} l mole^{-1} s^{-1}, respectively. An associative mechanism was proposed for these reactions since the formation rates are much faster than the ligand-water exchange process. The negative volumes of activation[40,41] obtained for the oxalate anation reactions as well as for cis-trans isomerisation of $Cr(H_2O)_2(C_2O_4)_2^-$ in water and mixed solvents further supported the associative interchange mechanism (I_a) type .

Espenson and Binau[42] reported the kinetics and mechanism of formation and aquation of hypophosphite-chromium(III) ion at 45-60°. The net rate of formation was given by equation below:

$$\frac{d\,[Cr\,H_2PO_2^{2+}]}{dt} = k_f\,[Cr^{3+}][H_3PO_2] - k_{aq}\,[Cr\,H_2PO_2^{2+}][H^+]$$

The values of the rate constants and their thermodynamic activation parameters were evaluated and compared with those of the kinetic data obtained for similar complexes previously.

Ceher and coworkers[43] studied the reaction between $Cr(H_2O)_6^{3+}$ and EDTA to form chromium(III)- EDTA complex spectrophotometrically. The rate was found to be dependent on the ligand concentration. They suggested that rate determining step was the transfer of ligand from outer-sphere to inner-sphere one. The apparent rate constant was the linear function of pH only within a narrow pH range. All the possible reaction paths at pH 2-10 were discussed by considering the stepwise protonation of EDTA and formation of various chromium(III) hydroxo species.

Duffy and Earley[44] studied the anation, water exchange and ion-pair formation of aquopentaammine-chromium(III) ion in acidic aqueous solutions containing chloride or thiocyanate ions. Thiocyanate ion was found to form more stable ion-pair and reacted more rapidly than chloride ion. Both anations were slow with respect to water exchange. The results were interpreted on the basis of the rate limiting loss of coordinated water followed by collapse of the solvation shell to fill the

vacancy created.

The equilibrium and kinetic studies of chromium(III) and chloride ions in methanol - water solutions were reported at 30, 40 and 60° by Baltisberger and King[14]. The rate at which methanol replaces water in the first coordination shell of chromium(III) ion was determined and was found to be very similar to the rate of exchange of water between solvent and the first coordination shell of chromium(III) ion in aqueous solution. The rate at which chloride ion dissociates from chromium(III) ion was found to be approximately tenfold lower than the replacement of methanol. Later on Baltisberger et al.[45] studied the thiocyanate anation of hexaaquochromium(III) and pentaaquomethanol-chromium(III) ions in water-methanol solvent with 0.308 mole fraction of methanol. The following mechanism was suggested.

$$CrO_6^{3+} + N^- \xrightarrow{k_1} CrO_5N^{2+} + O$$

$$CrO_5M^{3+} + N^- \xrightarrow{k_2} CrO_5N^{2+} + M$$

$$CrO_5M^{3+} + N^- \xrightarrow{k_3} \text{trans-}CrO_4MN^{2+} + O$$

$$CrO_5M^{3+} + N^- \xrightarrow{k_4} \text{cis-}CrO_4MN^{2+} + O$$

$$CrO_5N^{2+} + M \underset{k_7}{\overset{k_5}{\rightleftharpoons}} \text{trans-}CrO_4MN^{2+} + O$$

$$CrO_5N^{2+} + M \underset{k_8}{\overset{k_6}{\rightleftharpoons}} \text{cis-}CrO_4MN^{2+} + O$$

where M = CH_3OH, O = H_2O and N^- = SCN^- coordinated through nitrogen.

Nor and Sykes[46] studied the kinetics of complexing of oxalate to pentaammine-aquo-chromium(III) ion in the pH range 3-4 and temperature range 40-60°. The values of the rate constants do not differ significantly from the values obtained for the water exchange of the ion $Cr(NH_3)_5H_2O^{3+}$, this suggests that the reaction proceeds by a dissociative interchange mechanism. The following mechanism was proposed:

$$H_2C_2O_4 \underset{}{\overset{K_1}{\rightleftharpoons}} HC_2O_4^- + H^+$$

$$HC_2O_4^- \overset{K_2}{\rightleftharpoons} C_2O_4^{2-} + H^+$$

$$[Cr(NH_3)_5H_2O]^{3+} + C_2O_4^{2-} \overset{K'}{\rightleftharpoons} [Cr(NH_3)_5H_2O]^{3+}, C_2O_4^{2-}$$

$$[Cr(NH_3)_5H_2O]^{3+}, C_2O_4^{2-} \xrightarrow{k_1} \text{products}$$

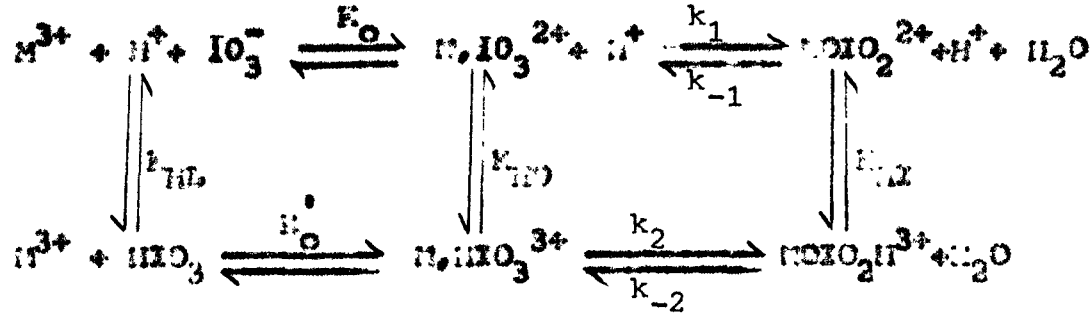
$$[Cr(NH_3)_5H_2O]^{3+} + C_2O_4H^- \overset{K''}{\rightleftharpoons} [Cr(NH_3)_5H_2O]^{3+}, C_2O_4H^-$$

$$[Cr(NH_3)_5H_2O]^{3+}, C_2O_4H^- \xrightarrow{k_2} \text{products}$$

The rate equation derived on the basis of above mechanism was:

$$\frac{k_{obs}}{[C_2O_4^{2-}]} = \frac{k_1 K' K_2 + k_2 K'' [H^+]}{[H^+] + K_2 + (K' K_2 + K'' [H^+]) [C_2O_4^{2-}]_T}$$

Sykes et al.[47] reported the temperature jump study of the rapid complexing of iodate with aquo-cobalt(III), chromium(III) and rhodium(III) ions at 25°. The following possible mechanism of associative nature was proposed:



The rate equation with respect to the above mechanism is:

$$\frac{1}{\tau} = \frac{(k_1K_o + k_2K_o'K_{HL}[H^+]_f)([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)}{1+K_{HL}[H^+]_f + (K_o+K_o'K_{HL}[H^+]_f)([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)} + \frac{k_{-1}+k_{-2}K_{HI}[H^+]_f}{1+K_{HI}[H^+]_f}$$

where K_{HL}, K_{HO} and K_{HI} are protonation constants and K_o and K_o' are outer-sphere formation constants.

S.T.D. Lo and D.W.Watts[48] studied the anation reactions of hexa(dimethyl sulphoxide) chromium(III) by $X^- = N_3^-$ and SCN^- in dimethylsulphoxide as a function of concentration, temperature and ionic strength in both conditions of X^- in excess over $Cr(Me_2SO)_6^{3+}$, and $Cr(MeSO)_6^{3+}$ in excess

over X^-, where greater certainty existed concerning the nature of solution species. The reactions were interpreted interms of dissociative interchange mechanism in which anation was probable result of dissociation only when the anion occupied a position in the first solvation sphere of the complex. The proposed mechanism is as follows:

$$Cr(Me_2SO)_6^{3+} + X^- \underset{}{\overset{K}{\rightleftharpoons}} Cr(Me_2SO)_6^{3+}, X^- \quad \text{(ion-pair)}$$

$$[Cr(Me_2SO)_6]^{3+}, X^- \xrightarrow{k} [Cr(Me_2SO)_5X]^{2+} + Me_2SO$$

On the basis of above mechanism the following rate law is derived:

(a) when the complex is in excess,

$$k_{obs} = k K [Complex] / (1+K [Complex])$$

(b) when the X^- is in excess there is a possibility of ion-triplet formation

$$X^- + [Cr(Me_2SO)_6]^{3+}, X^- \underset{}{\overset{K'}{\rightleftharpoons}} Cr(Me_2SO)_6^{3+}, 2X^-$$

(ion- triplet)

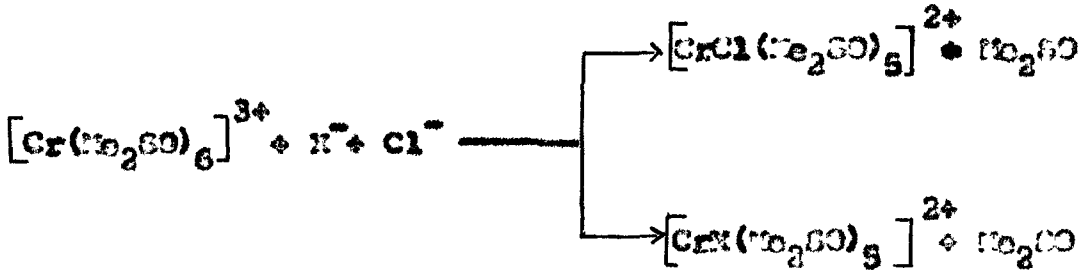
$$Cr(Me_2SO)_6^{3+}, 2X^- \xrightarrow{k'} Cr(Me_2SO)_5X^{2+} + X^- + Me_2SO$$

The overall mechanism for $[X^-]$ in excess yields:

$$k^{\circ}_{obs} = \frac{kK[X^-] + k'KK'[X^-]^2}{1+K[X^-] + KK'[X^-]^2}$$

Later S.T.D. Lo and D.J. Watts[47] made competitive anation studies with $[Cr(Me_2SO)_6]^{3+}$ in dimethyl sulphoxide.

The competitive anation reactions:



where X^- is N_3^- or SCN^-, had been studied in Me_2SO at one temperature as a function of the concentration of X^- and Cl^-. The results were compatible with a dissociative interchange (I_d) mechanism. It was observed that during the course of the reaction ion-pair as well ion- triplet formation occurs. The results were consistent with their previous results on the anation of $Cr(Me_2SO)_6^{3+}$ separately by SCN^-, N_3^- and Cl^-.

R.V. Swaddle and S.T.D. Lo[50] investigated the detailed mechanisms for anation, ion-pairing and solvent exchange of chromium(III) with various anionic ligands (X^-) in N,N-dimethyl formamide. Rate coefficients, enthalpies and entropies of activation were obtained for anation of $Cr(DMF)_6^{3+}$ in DMF by Br^-, NCS^- and ClO_4^-, as well as exchange rate data at single temperature in the presence of NCS^- and N_3^-. Ion-pair formation quotients were also estimated from the kinetics of one or both reactions for Br^-, Cl^-, NCS^-, N_3^- and ClO_4^-, the

last results superseding an earlier inaccurate estimate. They showed that the solvent- exchange rates were depressed slightly by ion-pairing and roughly to the same extent for all the above anions. On the basis of the experimental results they suggested an associative interchange (I_a) mechanism which is as follows:

$$Cr(DMF)_6^{3+} + X^- \underset{}{\overset{K_{IP}}{\rightleftharpoons}} \{Cr(DMF)_6^{3+}, X^-\}$$

$$\{Cr(DMF)_6^{3+}, X^-\} \xrightarrow{k_1} \{Cr(DMF)_5X\}^{2+} + DMF$$

$$\{Cr(DMF\text{-}d_7)_6^{3+}, X^-\} + 6DMF\text{-}h_7 \xrightarrow{k_1} \{Cr(DMF\text{-}h_7)_6^{3+}, X^-\} + 6DMF\text{-}d_7$$

$$Cr(DMF\text{-}d_7)_6^{3+} + 6DMF\text{-}h_7 \xrightarrow{k_2} Cr(DMF\text{-}h_7)_6^{3+} + 6DMF\text{-}d_7$$

Hence the rate equations derived are:

$$k_{obs} = k_1 K_{IP} [X^-]_F / (1+K_{IP} [X^-]_F)$$

$$k_{ex} = (k_1 K_{IP} [X^-]_F + k_2) / (1 + K_{IP} [X^-]_F)$$

Sykes et al.[51] studied the following reaction by temperature jump and stopped flow techniques:

$$Cr(EDTA)(H_2O)^- + X^{n-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cr(NH_3)_5SCN^{2+} + H_2O$$

They showed that the kinetic equilibrium constant $K_1 = k_f/k_b$ was in good agreement with those obtained spectrophotometrically.

Holba et al[52] studied the kinetics of aquopentaamminechromium(III) with thiocyanate ion. The ionic strength effect was studied on the rate and thermodynamic activation parameters of the reaction:

$$[Cr(NH_3)_5H_2O]^{3+} + SCN^- \longrightarrow [Cr(NH_3)_5(SCN)]^{2+} + H_2O$$

Reaction was first order and the rate decreased with increasing ionic strength.

Gangupta and Banerjea[53] studied the kinetics and mechanism of formation of $[Cr(BigH)_2(AA)]^{3+}$, from the reaction of cis-$[Cr(BigH)_2(OH_2)_2]^{3+}$ with 2,2'- dipyridyl or 1,10-phenonthroline. The reaction was found to be first-order with respect to the ligand concentration. Activation parameters were determined. They suggested that mechanism involves an outer-sphere association of the reactants followed by transformation and dissociation of the outer-sphere complex.

Sykes et al[54] studied the reaction between pentaammineaquochromium(III) with glycine and showed the evidences for a dissociative mechanism. The observation, that rate constants for 1^-, 2^- and zero charged reactants as well as glycine zwitterion were comparable, was indicative of $Cr-H_2O$ bond breaking being the dominant factor. The following mechanism was suggested:

$$\overset{+}{N}H_3CH_2COOH \underset{}{\overset{K_a}{\rightleftharpoons}} \overset{+}{N}H_3CH_2COO^- + H^+$$

$$[Cr(NH_3)_5H_2O]^{3+} + \overset{+}{N}H_3CH_2COO^- \xrightarrow{k_{obs}} Cr(NH_3)_5(OOCCH_2NH_3)^{3+} + H_2O$$

$$Cr(NH_3)_5(OOCCH_2NH_3)^{3+} \xrightarrow{H^+} Cr(NH_3)_4(H_2O)(OOCCH_2NH_3)^{3+} + NH_4^+$$

$$[Cr(NH_3)_5H_2O]^{3+} \cdot OOCCH_2\overset{+}{N}H_3 \underset{}{\overset{K_{IP}}{\rightleftharpoons}} Cr(NH_3)_5H_2O^{3+} \cdot {}^-OOCCH_2\overset{+}{N}H_3$$

$$Cr(NH_3)_5H_2O^{3+} \cdot {}^-OOCCH_2\overset{+}{N}H_3 \xrightarrow{k_{an}} Cr(NH_3)_5(OOCCH_2NH_3)^{3+} + H_2O$$

Hence,

$$k_{obs} = \frac{k_{an} K_{IP} K_a [Gly]_T}{[H^+] + K_a + K_{IP} K_a [Gly]_T}$$

Ramasami and Sykes[55] had discussed the mechanistic implications of kinetic data for the formation and equation of acedo - pentaammine chromium(III) complexes. They studied the formation of $Cr(NH_3)_5X^{2+}$, where $X^- = HCS^-$, CCl_3COO^-, Cl^-, Br^- and I^- from $Cr(NH_3)_5H_2O^{3+}$. Rate constants (k_f) for corresponding anation reactions have been obtained for all except X = I. They concluded that $Cr(NH_3)_5H_2O^{3+}$ exhibits more dissociative character than $Cr(H_2O)_6^{3+}$ in the substitution of H_2O.

Kornev and his coworkers[56] studied the kinetics and mechanism of the complex formation between hexaaquochromium (III) and nitrilodiacetic acid by spectrophotometry at pH=0.5-5.0

and μ = 0.1M. The reaction was first-order with respect to Cr^{3+} and LiI_2^- concentration. The activation energy calculated was 1.07×10^8 J/K mole. A mechanism was suggested in which the removal of one H_2O molecule from $[Cr(H_2O)_6]^{3+}$ inner-sphere was the rate-determining step.

Dushey and Stephenson[57] studied the substitution reactions of chloromethyl- and dichloromethyl- pentaaquo-chromium(III) ions and thiocyanate ion. Equilibrium and kinetic data were evaluated for the formation of 1:1 complex of NCS^- with $(H_2O)_5 Cr(CH_2Cl)^{2+}$ and $(H_2O)_5 Cr(CHCl_2)^{2+}$. The formation constants for NCS^- were found to be 10.4 and 12.8 M^{-1} for $CrCH_2Cl^{2+}$ and $CrCHCl_2^{2+}$, respectively. The kinetic data for anation followed the expression:

$$k_{an} = A[NCS^-]/(1 + C[NCS^-])$$

($A = k_1k_2/k_{-1}$ and $C = k_2/k_{-1}$)

and were consistent with both a limiting S_N1 and ion-pair mechanism.

Kinetic studies were carried out by Ohashi et al.[58] on the complex formation between aquachromium(III) ion and EDTA catalysed by $NaNO_2$ or Na_2SO_3 at 25 °C, ionic strength 0.5 M and pH = 3.5 - 4.80. It was observed that when concentration of EDTA or catalyst was in large excess over aquachromium(III) ion, the reaction to form Cr(III) - EDTA complex was first-

order with respect to the aquachromium(III) ion concentration and the rate increased with increasing concentration of EDTA or catalyst.

Stanivas et al.[59,60] studied the kinetics and mechanism of complex formation between hexaquochromium(III) and trimeta, tetrametaphosphate anions. The effects of ionic strength and temperature on the rate were observed. They proposed an ion-pair mechanism of I_d type. The reaction was found to be first-order. The activation parameters were evaluated.

Kimura and Ohirai[61] studied the kinetics of the reaction between ethylenediaminetetra-acetate (EDTA) with aquochromium(III) ion in mixed solvents of water and methanol, ethanol in pH range 3.3-4.6 . The reaction was observed to be first-order with respect to the chromium(III) concentration and proceeded only through dissociation of coordinated water molecules out of hexaaquochromium(III) and hydroxopentaaquo-chromium(III) ions. The rate of the reaction was independent of EDTA concentrations. The following mechanism was suggested:

$$Cr(H_2O)_6^{3+} \rightleftharpoons Cr(OH)(H_2O)_5^{2+} + H^+ \quad K_a$$

$$Cr(H_2O)_6^{3+} \xrightarrow[(EDTA)]{k_1} Cr(edta)(H_2O)^- + 5H_2O$$

$$Cr(OH)(H_2O)_5^{2+} \xrightarrow[(EDTA)]{k_2} Cr(edta)(H_2O)^- + 4H_2O + OH^-$$

and the rate law derived on the basis of above mechanism was found:

$$\frac{d[Cr(edta)(H_2O)^-]}{dt} = k_1[Cr(H_2O)_6^{3+}] + k_2[Cr(OH)(H_2O)_5^{2+}]$$

$$= \frac{k_1 + k_2 K_a / [H^+]}{1 + K_a / [H^+]}[Cr(III)_{aq}]$$

where $[Cr(III)_{aq}] = [Cr(H_2O)_6^{3+}] + [Cr(OH)(H_2O)_5^{2+}]$

$$k_{obs} = \frac{k_1 + k_2 K_a / [H^+]}{1 + K_a / [H^+]}$$

The values of k_1, k_2 and K_a were determined. k_1 and k_2 were independent of the concentrations of alcohols. K_a was slightly decreased with increasing concentrations of alcohols. They made important observations that hydroxopentaaquochromium (III) is more labile than hexaaquochromium(III) by a factor of 10^2. Catalytic effects on the reaction rate were also found. Additions of small amounts of hydrogen peroxide and iron (II) or peroxodisulphate and iron (II) to the reaction

solution accelerated reactions 3-5 times between EDTA and aquachromium(III) ions in aqueous solution.

Mandal and Lee[62,63] studied the kinetics of the substitution of aqua ligands from hexaaquochromium(III) ion by 2,2'- dipyridyl and 1,10-orthophenanthroline in water-ethanol mixtures. The following rate law was established:

$$\text{Rate} = k_2 \left[Cr(H_2O)_6^{3+}\right] \left[\text{Ligand}\right]$$

The reaction for substitution was found to be pH dependent but independent of ionic strength. Activation parameters for the reaction path (k_2) were calculated and were compared with the water exchange rate on the basis of which an associative mechanism was proposed.

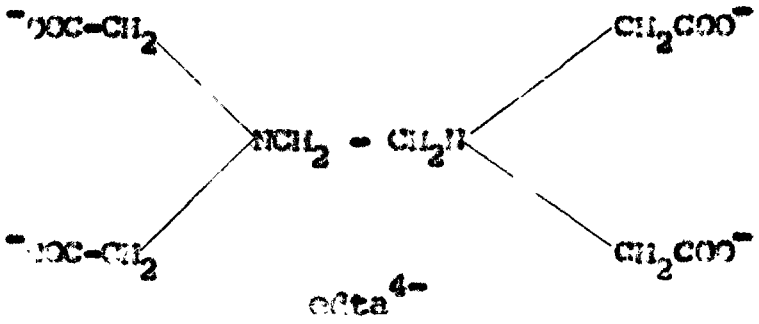
Orhino et al.[64-69] have studied the equilibrium and kinetics of the reactions:

$$\left[Cr\,Y(H_2O)\right]^{(n-3)-} + X \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \left[Cr\,X\,Y\right]^{(n-2)-} + H_2O \qquad (1)$$

where X represents,

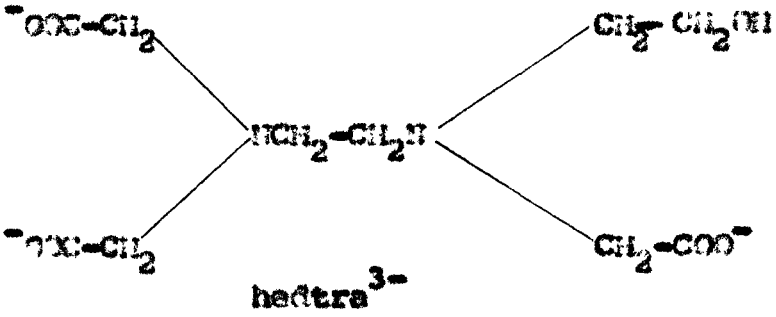
$$X = N_3^-,\ OAc^-,\ NO^-\ \text{and}\ NCS^-$$

and Y represents ,



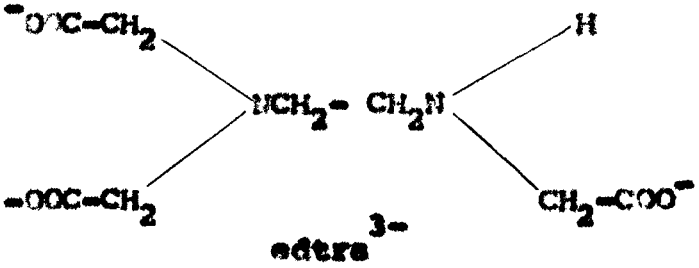
edta^{4-}

(ethylenediamine - N,N,N',N' - tetraacetate)



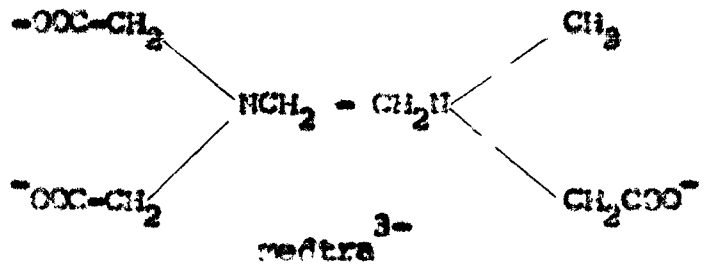
hedtra^{3-}

(N-(hydroxyethyl)ethylenediamine - N,N,N' - triacetate)

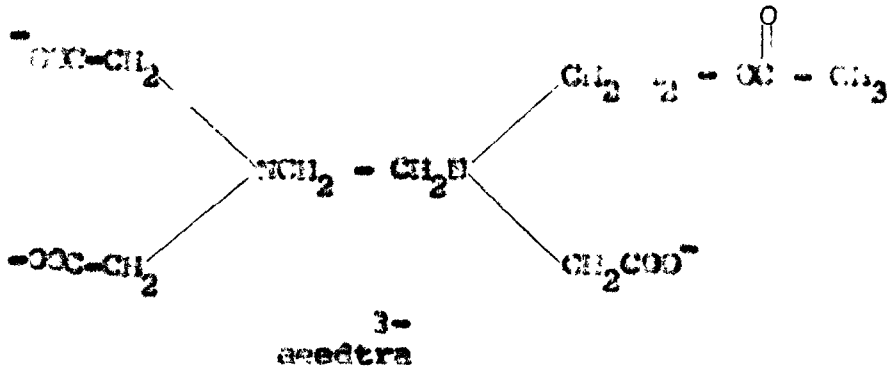


edtra^{3-}

(ethylenediamine - N,N,N' - triacetate)



(N-methylethylenediamine - N,N',N'- triacetate)



(N-(acetoxyethyl)-ethylenediamine-N,N',N'- triacetate)

; n is 4 for edta and 3 for hedtra, edtra, medtra and aeedtra.

They found that the formation constants of $[CrXY]^{(n-2)-}$ increase in the following order with the nature of the X^-: Br^-, $Cl^- < ONO^- < NCS^- \backsim OAc^- < N_3^-$. The order seems not to be related directly to that of the basicity of the X^-.

The rate constants of the reaction (1) are compared with those of the corresponding reactions of pentaaquo-and pentaamminochromium(III) complexes in Tables 6 and 7 .

TABLE-6. Anation Reaction Rate Constants ($k_f M^{-1}$, s^{-1})

	X⁻					
Complex	N_3^-	OAC^-	OXO^-	NCS^-	Cl^-	Br^-
$[Cr(H_2O)_6]^{3+}$				1.8×10^{-6}[a]	3.1×10^{-8}[b]	8.6×10^{-9}[c]
$[Cr(NH_3)_5(H_2O)]^{3+}$	9.0×10^{-6}[d]	1.0×10^{-5}[d]		1.5×10^{-3}[d,e]	8.4×10^{-5}[d,e]	7.3×10^{-5}[f]
$[Cr(edtra)(H_2O)]$		$(2.88\pm0.14)\times10^{-2}$[g]		$(2.95\pm0.1)\times10^{-2}$[h]		
$[Cr(medtra)(H_2O)]$		$(7.31\pm0.35)\times10^{-4}$[g]	$(1.7\pm0.3)\times10^{-3}$[h]			
$[Cr(hedtra)(H_2O)]$	19.8 ± 1.2[h]	7.60 ± 0.61[g]	12 ± 2[h]	3.32 ± 0.11[h]	0.1[i]	0.2[i]
$[Cr(emedtra)(H_2O)]$		4.5 ± 0.7[j]				
$[Cr(Hedta)(H_2O)]$				0.773 ± 0.042[h]		
$[Cr(edta)(H_2O)]^-$	98 ± 5[k]	3.3 ± 0.4[g]		13.7 ± 0.6[h]		

[a]Ref.10. [b]T.W.Swaddle and E.L.King, Inorg.Chem., 4 (1965) 532. C.F. Hale and E.L.King, J.Phys.Chem., 71 (1967), 1779.
[c]F.A.Guthrie and E.L. King, Inorg. Chem., 3 (1964) 916; J.H. Espenson and E.L. King, J. Phys. Chem., 64 (1960) 380.
[d]D.A. House, Coord. Chem. Rev., 23 (1977) 223. [e]I = 0.11 M.
[f]Ref.55. [g]Ref.64. [h]Ref.68. [i]Ref.66. [j]Ref.67. [k]Ref.81.

TABLE-7. Aquation Reaction Rate Constants (k_h, M^{-1} s^{-1})

Complex	X^-					
	N_3^-	OAc^-	OH^-	NCS^-	Cl^-	Br^-
$[CrX(H_2O)_5]^{2+}$	4.1×10^{-8}	4.1×10^{-7}		9.2×10^{-3}[c]	2.8×10^{-7}[a]	4.3×10^{-6}[a]
$[CrX(NH_3)_5]^{2+}$	3.6×10^{-8}			2.7×10^{-3}[a,e]	7.4×10^{-6}[a]	3.1×10^{-5}[f]
$[CrX(edtra)]^-$		$(1.63\pm0.13)\times10^{-3}$[g]		$(2.40\pm.17)\times10^{-3}$[h]		
$[CrX(medtra)]^-$		$(5.83\pm0.23)\times10^{-3}$[g]	$(3\pm3)\times10^{-4}$[h]			
$[CrX(hedtra)]^-$	0.189 ± 0.012[h]	0.450 ± 0.030[g]	6.24 ± 0.34[h]	0.244 ± 0.019[h]	0.697 ± 0.044[i]	2.0[i]
$[CrX(emedtra)]^-$		0.38 ± 0.06[j]				
$[CrX(Hedta)]^-$				$(3.17\pm0.33)\times10^{-2}$[h]		
$[CrX(edta)]^{2-}$	13.4[k]	5.4 ± 0.6[g]		26.3 ± 3.9[h]		

[a]J.O. Edward, and G. Ortaggi, Inorg. Chem. Acta, 11 (1974) 47. [b]E. Deutsch and H. Taube, Inorg. Chem., 7 (1968) 1532. [c]Ref. 10. [e]I = 0.07M. [f]Ref.55. [g]Ref.64. [h]Ref.68. [i]Ref.66. [j]Ref.67. [k]Ref. 51.

The k_f values which correspond to the rate constants of the anation reactions are not so sensitive to the change of nature of Y^-. For the given anion Y^-, however, the change of the kind of chromium(III) complexes gives strikingly large changes of the rate constants. The order of reactivities is $[Cr(H_2O)_6]^{3+} < [Cr(NH_3)_5H_2O]^{3+} << [Cr(medtra)(H_2O)] < [Cr(edtra)(H_2O)] << [Cr(hedta)(H_2O)] < [Cr(aeedtra)(H_2O)] \cdot [Cr(hedtra)(H_2O)] \cdot [Cr(edta)(H_2O)]^-$.

The substitution reactions of chromium(III) complexes in this work are very rapid in comparision with both the acidopentaaquo- and acidopentaamminchromium(III) complexes. The results are explained on the basis that coordination of Y^{n-} reduces the positive charge of the central chromium(III) ion and leads to loosening of the $Cr-OH_2$ bond. The N-substituent groups in the $[Cr(edtra)(H_2O)]$ and $[Cr(medtra)(H_2O)]$ complexes have no coordinating ability for the metal ions. On the other hand, when the N substituent groups of Y^{n-} have coordinating ability, such as CH_2COOH, CH_2CH_2OH, $CH_2CH_2OCOCH_3$, or CH_2COO^-, the k_f values are much larger than those of the $[Cr(edtra)(H_2O)]$ and $[Cr(medtra)(H_2O)]$ complexes. This fact suggests strongly that the $Cr-OH_2$ bond rupture is accelerated by the transient coordination of these pendant groups to central chromium(III) ions.

The k_b values which correspond to the rate constants of the aquation reactions are also relatively insensitive to

the change of the nature of the X^-. The order of the reactivities of the aquation reactions is very similar to that of the anation reactions. Therefore a situation similar to that considered for the anation reactions may also exist for the aquation reactions.

Ridik and coworkers[6] produced mechanistic informations from the effect of pressure on the kinetics of some anation reactions of aquapentaamminecobalt(III), -rhodium(III) and -chromium(III) ions in acidic aqueous solutions. The anations of $Co(NH_3)_5H_2O^{3+}$ by Cl^- and SO_4^{2-}, $Rh(NH_3)_5H_2O^{3+}$ by Cl^- and $Cr(NH_3)_5H_2O^{3+}$ by NCS^- were studied in acidic aqueous solution as a function of nucleophile concentration and pressure upto 1.5 k bar. No kinetic evidence for participation of ion-pairs could be obtained. The volumes of activation for the anation reactions were + 1.4±0.8 (μ=2M, 60°), +2.3± 1.8 (μ = 2M, 60°), + 3.0±0.7 (μ = 2 M, 60°), and -4.9± 0.6 $cm^3 mole^{-1}$ (μ = 1M, 50°), respectively. These values were used in conjunction with the volumes of activation for the corresponding aquation reactions to estimate the overall volume changes incurred in the reactions. The later could then be compared with independently obtained values of $\Delta\bar{V}$. The results were discussed interms of an interchange mechanism and compared with the data reported in the literature.

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Miguel Herrer and Sykes reported the studies on the kinetics and mechanism of the reaction of phosphate (H_3PO_4 and $H_2PO_4^-$) with aquapentaamminechromium(III). The reaction (pH=1-3) yielded the phosphato-complex $Cr(NH_3)_5H_2PO_4^{2+}$ which is stable to further reaction (including NH_3 loss) at temperatures 40-60°C investigated. From the kinetics (μ = 1.00 M, $HClO_4$) evidence was obtained for outer-sphere association of H_3PO_4 (K_1=0.32 M^{-1}), $H_2PO_4^-$ (K_2=1.8 M^{-1}) with $Cr(NH_3)_5H_2O^{3+}$ where K_1 and K_2 showed a little dependence or no dependence on the temperature. Rate constants for interchange leading to the formation of phosphato complex were as far as could be ascertained identical ($k_1=k_2$), with $k(50°C) = 1.45\times10^{-4}$ s^{-1}, $\Delta H^* = 25.0$ kcal $mole^{-1}$, and $\Delta S^* = 1.1$ cal K^{-1} $mole^{-1}$. Comparisons were made with other studies involving $Cr(NH_3)_5H_2O^{3+}$ as well as $Cr(H_2O)_6^{3+}$. Reactivity patterns for $Cr(NH_3)_5H_2O^{3+}$ were intermediate between those for $Cr(H_2O)_6^{3+}$ on the one hand (Ia assignment) and $Co(NH_3)_5H_2O^{3+}$ and other 2^+ aquo ions on the other hand (Id) . The previously determined volume of activation for H_2O exchange on $Cr(NH_3)_5H_2O^{3+}$ had been interpreted in terms of an Ia assignment. This was consistent with reactivity patterns only if it was accepted that plots of log k_{aq} against log-(K_{IS} K_{os}) yielded slopes of 1.0 for an Id mechanism and less than 1.0 for an Ia mechanism.

Tyagi and Khan[71-74] investigated the kinetics and mechanism of anation of hexaaquo-chromium(III) by a variety of carboxylic acids both in water and water-ethanol mixtures under varying conditions of temperature, ionic strength, pH, solvent composition and ligand concentration. On the basis of experimental results an associative interchange (I_a) mechanism was suggested.

Hallen and his coworkers[75] studied the kinetics of anation of cis-diaqua(ethylenediamine) (oxalato) chromium(III) complex ion by oxalato species under the varying conditions of temperature, pH, ligand concentration and ionic strength. Observed pseudo-first-order rate constants exhibited a complex hydrogen ion dependence and a mass law retarded first-order dependence on the formal oxalate concentration. The following associative interchange (Ia) mechanism was suggested:

$$H_2C_2O_4 \underset{}{\overset{K_1}{\rightleftharpoons}} H^+ + HC_2O_4^-$$

$$HC_2O_4^- \underset{}{\overset{K_2}{\rightleftharpoons}} H^+ + C_2O_4^{2-}$$

$$cis\text{-}Cr(ox)(en)(H_2O)_2^+ \underset{}{\overset{K_{a1}}{\rightleftharpoons}} Cr(ox)(en)(OH)(H_2O) + H^+$$

$$cis\text{-}Cr(ox)(en)(H_2O)_2^+ + HC_2O_4^- \underset{}{\overset{K_B}{\rightleftharpoons}} (IP\text{-}1)$$

$$cis\text{-}Cr(ox)(en)(H_2O)_2^+ \underset{}{\overset{K_c}{\rightleftharpoons}} (IP\text{-}2)^-$$

$$(IP\text{-}1) \underset{}{\overset{K_2'}{\rightleftharpoons}} (IP\text{-}2)^- + H^+$$

$$(IP\text{-}1) \xrightarrow{k_1} Cr(ox)_2(en)^- + H_3O^+ + H_2O$$

$$(IP\text{-}2) \xrightarrow{k_2} Cr(ox)_2(en)^- + 2\,H_2O$$

The observed rate constant derived for Ia mechanism is given by the equation:

$$k_{obs} = \frac{k_1 K_c[H^+] ([H^+] + K_2^*)[C_2O_4^{2-}]}{K_2^*[H^+] + K_{a1} + K_c[H^+] ([H^+] + K_2^*)[C_2O_4^{2-}]}$$

where K_2^* is the acid dissociation constant of an associated hydrogen oxalato ion and K_{a1} is the first acid dissociation constant of the aqua ligands of the complex ion. A two step oxalate anation mechanism has been described for this complex ion and other oxalato complexes of chromium(III). The mechanism was initiated by one ended dissociation and isomerization of an oxalato-O,O* ligand to oxalato-O,O bonding mode. Associative interchange of an ion paired oxalate species for an aqua ligand was proposed to occur in the second step as a direct consequence of ligand isomerization. The mechanism successfully explained differences in the nature of activation parameters for oxalate anation of oxalato-complexes of chromium(III). It also generalised to provide a water exchange mechanism for oxalato complexes of chromium(III) which did not limit the anation rate.

Biological Activity of Chromium

Chromium(VI) compounds such as chromates, dichromates and particularly chromic acid acts as irritants of the skin and mucous membranes. Dermatitis results in the cases of some individuals who have become sensitised and allergic to

Cr(VI) compounds. In plants where such compounds are produced, many precautions are taken to prevent exposure to their dusts and mists. There is no evidence that Cr(III) compounds have any toxic effects.

On the contrary, chromium, as Cr(III), appears to be an essential trace metal in mammalian metabolism. The first demonstration of metabolic effect of chromium was reported by Mertz and Schwarz in 1955.[76] In the meantime, a great deal of evidence pointing to the essentiality of chromium has been obtained, much of it by Mertz and his associates and by Schroeder's group, a summary of which is given in the following:

When analytical methods of sufficient sensitivity (e.g. atomic absorption, activation analysis) are used, essentially all biological materials are found to contain chromium. A brief summary of its distribution in water, soils and biological tissues is given in Table 8 . Chromium is not well absorbed in the intestinal tract; Cr^{6+} is absorbed better than the biologically active Cr^{3+}. It is presumably transported by the blood protein siderophilin, which is also the carrier of iron. Chromium is excreted mainly in the urine and to a smaller extent in feces.

TABLE-8. Distribution of Chromium[76]

Material	Cr (ppm)[a]
Soils	5-3000[b] (median, 100)
Igneous rocks	100
Shales	90
Sandstones	35
Coal	60
Fresh water	0.0001-0.08 (median, 0.00018)
Sea water	0.00005
Land plants	0.230
Marine plants	1.0
Land animals	0.075
Marine animals	0.2-1.0
Plant tissues	0.8-3.5
Mammalian tissues	0.025-0.85
Hard tissues (marine organism)	0.2-0.85
Mammalian blood	0.260
Plasma	0.240
Red cells	0.0015[c]

[a]Results for soils and biological materials reported on oven-dried basis.

[b]Highest in soils derived from basalt and serpentin

[c]120 Cr atoms per red cell

Testes, bones, liver and spleen have a high affinity for chromium while the affinity of muscle and brain is low. Chromium(III) coordinates with proteins. Since chromates penetrate walls of red cells, CrO_4^{2-} [77] is used to label erythrocytes. Hacker and Valee[78] found high concentrations of several metals, including chromium, in beef liver RNA.

There is a close dependence of biological effect of chromium (as Cr(III)) on the presence of insulin, the apparent effect of chromium supplementation in diets depends on the existence of a deficiency state, and there is a narrow dose range for optimum effect. The effects of chromium deficiency in rats and monkeys include impaired glucose tolerance, decreased glycogen reserve, increased incidence of aortic lesion, disturbance in utilization of amino acids in protein synthesis and a syndrome resembling diabetes. The effect of chromium supplementation are manifested in numerous ways including the following: increased survival of rats and mice; prolonging of survival of old animals; increase in growth rate of rats and mice raised in a controlled environment.

Roginski and Mertz[79-81] found that in 10-15% of the rats fed a diet deficient in both protein and chromium (100 ppb), a visible eye lesion develops which results in opacity of cornea in one or both eyes; although this is prevented by sufficient chromium in the diet, the fully

developed defect is not reversed by feeding chromium, high protein or both.

Considerable work has been done directly relevant to metabolic role of chromium in human beings (e.g. investigations of Hertz, Tuffy, Jenkins and Schroeder). It has been found that supplementation improves or normalises impaired glucose tolerance of some diabetics, old people and malnourished children, but not of others. It has become evident that, although low chromium states exist, they are not the sole cause of impaired glucose tolerance. The known worsening of glucose tolerance among women who have had several children may be related to chromium depletion. Hambidge[82] has shown that the chromium content of hair of mothers is less than a third of that nulliparae.

Hertz and associates have utilized in vitro techniques for evaluating chromium compounds with respect to relation between chemical composition of chromium compounds and their biological effects. These comprise comparing the rates of utilisation of ^{14}C-tagged glucose by epididymal tissue from diabetic rats in the presence of insulin with and without added chromium. The most stable complexes such as $Cr(acac)_3$ (acac = acetylacetonate) are relatively ineffective while less stable complexes (such as those of ethylenediamine, methionine etc.) enhance the action of insulin. Outstanding

activity is manifested by the glucose tolerance factor (GTF), a chromium complex is extracted from brewer's yeast and pork kidney powder (both in vitro and vivo).

An ultimate objective in this area is to write a series of equations for all reactions that Cr(III) undergoes from absorption to excretion. It is assumed that the final biologically effective form of chromium is produced as a result of a sequence of reactions of Cr(III) with ligands present in biological system. Specifically it is essential to determine which of the many biological substances are most likely to maintain Cr(III) in transportable (and presumably available) form.[33]

Reactions of Chromium(III) with Biological Ligands

Ingested chromium(III) is presumably converted to its ultimate biologically active chemical form by a sequence of reactions with biological ligands in the mammalian system. The principles outlined above may be applied to this extremely chemical system.[84,85] In media of physiological pH, the expected reaction of Cr(III) is olation except as it may be prevented or minimized by competition of ligands other than OH^-. It may be assumed that extensive olation would render Cr(III)

biologically unavailable since this reaction would presumably be irreversible under relatively mild conditions of biological system.

It may therefore be assumed that the chemical form and concentration of biologically active chromium will be determined by competition of Cr(III) by H^+ and other ligands of biological system. One of the net results of the competition will be the establishing of the average state of aggregation of Cr(III) product(s) which will be characteristic of a given reaction mixture under a given set of reaction conditions. The rate of transport of Cr (III) through a membrane will be a function of the state of aggregation. This has been investigated by method of sequential dialysis.[83] In this procedure successive samples of Cr(III)- ligand reaction mixture buffered at physiological pH are dialysed at intervals and curves are plotted showing functional attainment of dialysis equilibrium vs. time. The area under the dialysis curve is proportional to the rate of diffusion of the Cr(III) and thus inversely proportional to the molecular size of the diffusing species; it is, therefore a measure of the effectiveness of the ligand in preventing polymerisation (i.e. of the ligand's coordinating tendency). The area progressively decreases when the ligand has relatively low coordinating tendency. With the most effective ligands, the area under the curve is a minimum and

remains constant for a long time (e.g. 2-3 weeks). Typical results are shown in Fig.2 (phosphate buffer only, no effective ligand in reaction mixture) and Fig.3 (same reaction mixture containing methionine, an effective ligand).

Since the fractional decrease in the area under the dialysis curve as the reaction mixture ages is inversely proportional to the coordinating ability of the ligand, this procedure makes it possible to establish the orders of relative coordinating tendencies. This has been done with many biological ligands, including nearly all the compounds of Krebs cycle, most of the compounds of the glycolysis chain, numerous amino acids and various biological phosphates. The order of the coordinating tendencies of the Krebs cycle compounds for example, is: Citrate > isocitrate > malate > oxalacetate > α- ketoglutarate > aconitate > fumarate > succinate. Of many biological ligands tested, among the most effective (as determined by sequential dialysis) are histidin, ATP, ADP, thiamine pyrophosphate, fructose - 1, 6- diphosphate, 3 - phosphoglycerate, citrate, isocitrate and tartonate. [83,86]

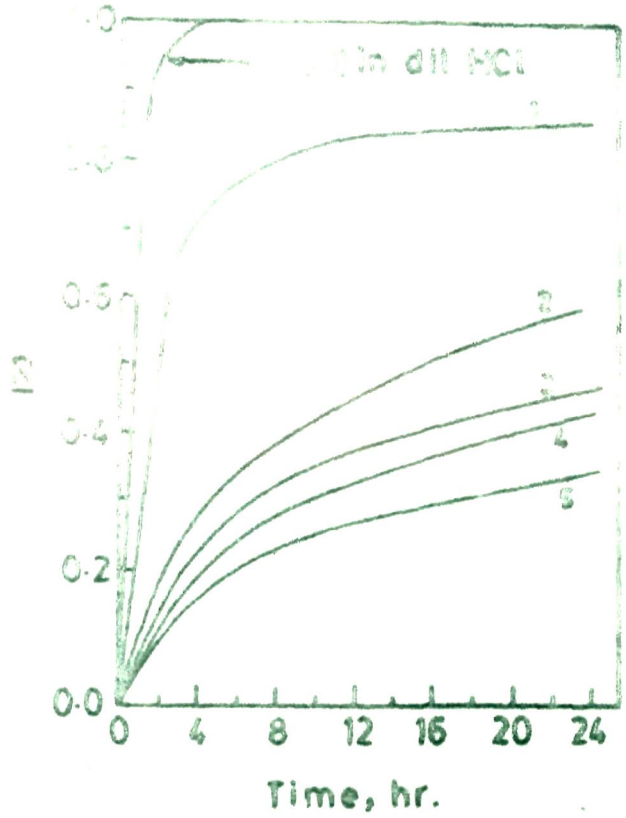

Fig. 2: Sequential dialysis: $[Cr^{3+}] = 1 \times 10^{-4}$ M, $[PO_4^{2-}] = 0.02$ M, pH = 7.4. Reaction mixture aged: 1, 1 hr; 2, 24 hr; 3, 1 week; 4, 2 weeks. 5, 4 weeks. R, fractional attainment of dialysis equilibrium in closed-system two-component dialyzer.

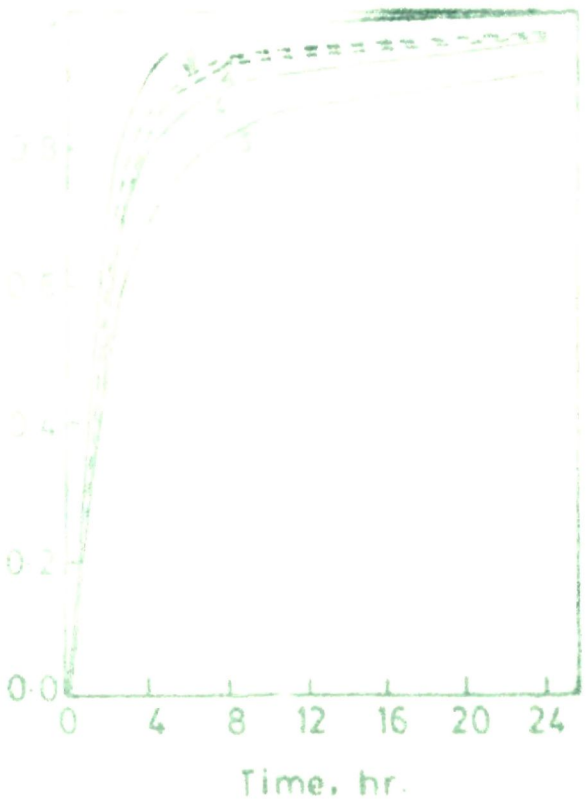

Fig 3: Sequential dialysis: $[Cr^{3+}] = 1 \times 10^{-4}$ M, $[PO_4^{3-}] = 0.02$ M, pH = 7·4; ligand–methionine. [Methionine], aging of reaction mixture: 0·1 M: 1, 1 hr. 24 hr. 1 week; 0·05 M: 2, 1 hr. 3, 24 hr.; 0·01 M: 4, 1 hr. 5, 24 hr. R, fractional attainment of dialysis equilibrium in closed-system two-component dialyzer.

Nature of Research Work Described in this Dissertation

In going through the literature on the kinetics and mechanism of substitution reactions of chromium (III) complexes and specially the aquation reactions it was observed that the number of such studies with amino acid ligands were very limited. Therefore, a thorough systematic work is required in this field. With this view the work on the interaction of hexaaquochromium(III) in aqueous medium was carried out with various amino acids (Glycine, DL-α-Alanine, DL-Valine, DL-Serine, DL-Methionine and DL-Aspartic acid). The studies were done under the following conditions:

(I) Different concentrations of ligands

(II) Different concentrations of hydrogenions

(III) Different ionic strengths

(IV) Different temperatures

The kinetic results were analysed for each reaction separately and their mechanisms were proposed. These studies are reported in this thesis.

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CHAPTER - XI

CONCLUSION

CHAPTER - II

EXPERIMENTAL

Chemicals.

Amino acids (glycine-CLIMAX, Czechoslovakia, DL-α-alanine-SRL, India, L-valine-[illegible], DL-serine-SRL, India, DL-methionine, L-threonine and DL-aspartic acid-SRL, etc.) were used without further purification. Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) was of AnalaR quality. Potassium nitrate (BDH, India) was used to adjust ionic strength of solutions. Strengths of stock solutions of nitric acid (AnalaR) and sodium hydroxide (BDH, India) were checked by acid-base titrations. For this purpose sodium hydroxide was standardized by titrating with a standard solution of oxalic acid and then HNO_3 was titrated with this standard alkali solution. All other chemicals used were reagent grade.

All the solutions were prepared in deionized, air-free, doubly distilled water. Distillation was performed in an all glass apparatus.

Standardisation of Chromium Nitrate Solution.

Stock solution of chromium nitrate was standardised by two independent methods- (i) ion exchange method,[1] and (ii) iodometric method.[2]

Total concentration of chromium nitrate in stock solution by the ion-exchange method was estimated by elution through a

cation exchanger (Dowex 50-X8) in the H^+ form and titrating the HNO_3 in the effluent with standard alkali. The free acid content of stock solution of Cr(III) was then evaluated.

In the iodometric method chromium nitrate was oxidized to dichromate by boiling with a solution of potassium persulphate. The oxidising agent was taken in excess. Silver nitrate was used to catalyse the reaction. The excess of persulphate was destroyed by prolonging the boiling for a short time after oxidation of chromium to the dichromate conditions had been judged to be complete. The dichromate solution was then cooled and diluted to a definite volume. Its concentration was determined with reference to a standard solution of ferrous sulphate.

Determination of Composition of Complexes.

Compositions of the complexes formed by the interaction of $Cr(H_2O)_6^{3+}$ with different amino acids were determined by Jobs method[3] of continuous variations.

Kinetic measurements.

The kinetics of reactions of aminoacids with $Cr(H_2O)_6^{3+}$ were followed spectrophotometrically under pseudo-first order conditions with the ligand in excess with respect to the metal ion. The pH was varied from 2.9 to 4.5 at μ = 1M (except when the effect of μ was studied). The pH of the

experimental solutions were adjusted by adding requisite amounts of 0.05M HNO_3 / NaOH solution.

The requisite volumes of all the reactants except chromium nitrate, were taken in a three necked reaction vessel fitted with a double walled condenser (see Fig.1) to check any evaporation. An appropriate concentration of potassium nitrate was added to maintain the ionic strength. The reaction mixture was then thermostated in a water bath at the desired temperature within a precision of ± 0.1°. An inert atmosphere inside the vessel was maintained by bubbling nitrogen gas which also ensured thorough mixing. Reaction was then started by adding requisite amount of chromium nitrate (which was kept thermostated at the same temperature in a separate flask). Aliquots of reaction mixture were pipetted out at definite time intervals and the reaction was quenched by cooling in ice bath and then A_t was measured at 540 nm (for all the amino acids except for aspartic acid which was done at 530 nm). A_∞ was obtained by direct measurement of the experimental solutions kept long enough for the reaction to be complete. The optical density of $Cr(H_2O)_6^{3+}$ in a solution as above without any added ligand was taken as Ao.

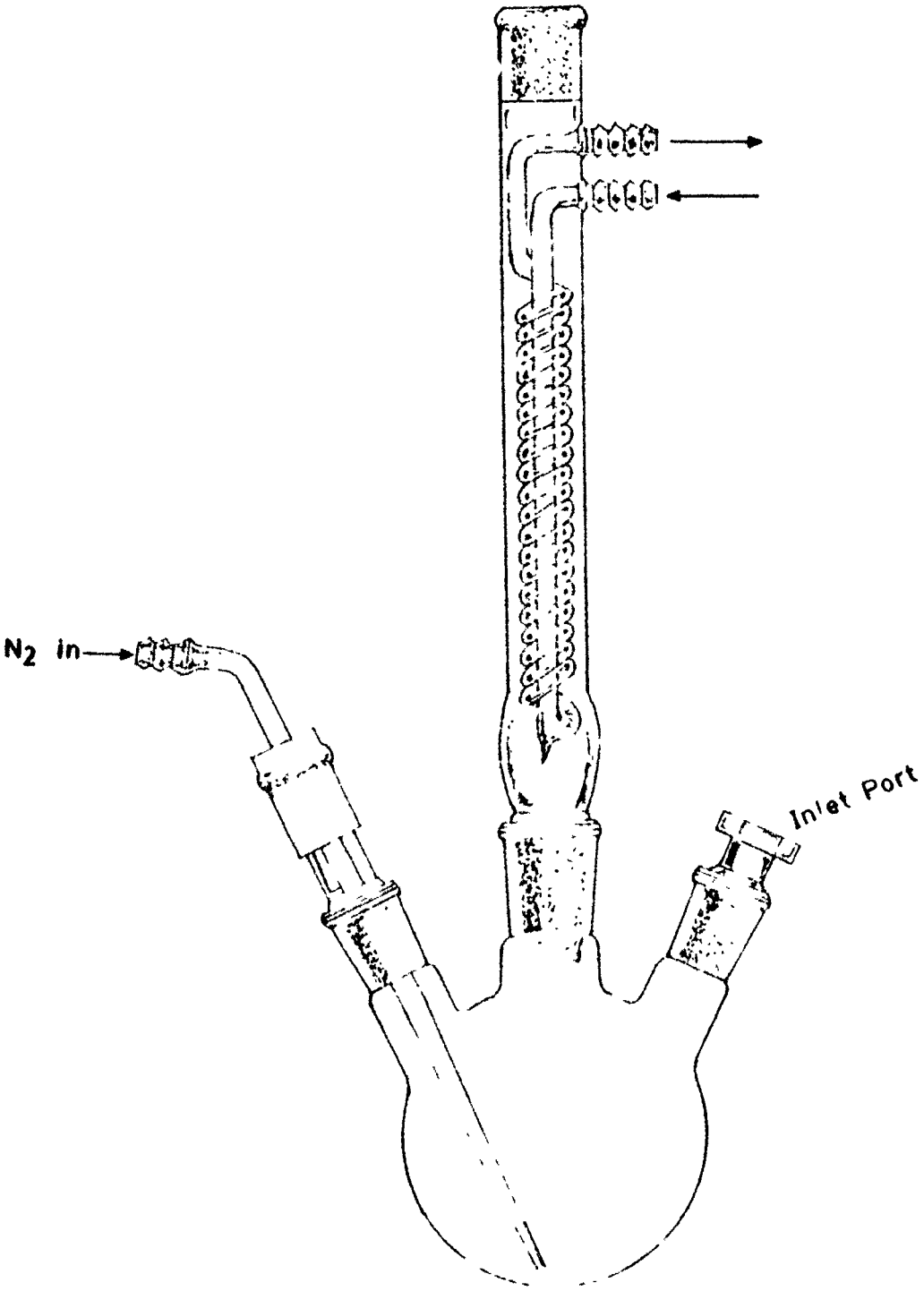

FIG.1 : THREE-NECKED FLASK FITTED WITH A DOUBLE WALLED CONDENSER

Calculations

The pseudo- first order rate constant , k_{obs}, was determined from equation (1).

$$A_t = A_\infty - (A_\infty - A_o)\ e^{-k_{obs}} \qquad (1)$$

where A is the absorbance and subscripts refer to time. A computer programme in FORTRAN IV was made for the calculation of k_{obs}, which is listed in Appendix (Programme No.1)

The kinetics of hexaaquochromium (III) with different amino acids were performed under varying conditions of ligand, ionic strength, pH and temperature. The results are given in Chapter IV.

Apparatus

Absorbance measurements were obtained with Bausch & Lomb spectronic - 20 colorimeter.

An ELICO pH-meter model LI-10 (Hyderabad, India) employing a glass electrode (ELICO , Type EK- 62A) and calomel electrode (ELICo , Type ER-70) was used to measure the pH of the solutions.

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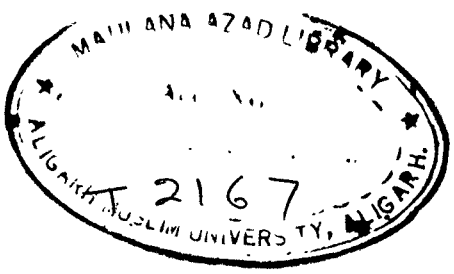
2. A.I. Vogel, "A Text book of quantitative inorganic chemistry", Longman's, Green and Co., London, 2nd Ed. (1951) p. 453.

3. W.C. Vosburg and G.R. Cooper, J. Am. Chem. Soc., 63 (1941) 437.

CHAPTER - III

GENERALITIES



CHAPTER - III

G E N E R A L I T I E S

STRUCTURAL FORMULAS, IONIZATION AND FRACTIONAL DISTRIBUTION OF DIFFERENT SPECIES IN THE AMINO ACIDS USED.

The structural formulas of the amino acids used in the present study are given in the Table 1 alongwith their pK values:

TABLE-1. Structural Formulas and pK Values of Different Amino Acids.

Amino acid	Structure	pK(25°c)[1,2]		
		α- COOH gp.	β-COOH gp.	α-NH_3^+ gp.
Glycine	H_2N-CH_2-COOH	2.40		9.80
Alanine	$H_2N-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-COOH$	2.30		9.90
Valine	$H_2N-\underset{\displaystyle H_3C-\underset{\displaystyle H}{\underset{\vert}{C}}-CH_3}{\underset{\vert}{CH}}-COOH$	2.30		9.60
Serine	$H_2N-\underset{\displaystyle CH_2OH}{\underset{\vert}{CH}}-COOH$	2.10		9.20
Methionine	$H_2N-\underset{\displaystyle (CH_2)_2SCH_3}{\underset{\vert}{CH}}-COOH$	2.28		9.21
Aspartic acid	$H_2N-\underset{\displaystyle \underset{\displaystyle COOH}{\underset{\vert}{CH_2}}}{\underset{\vert}{CH}}-COOH$	2.00	3.90	10.00

It is well known that monoamino, monocarboxylic acids take the following ionised forms in acidic, neutral, and alkaline ranges (written for the simplest amino acid - glycine):

$$\overset{+}{N}H_3 - CH_2 - COOH \underset{(H_2L^+)}{\overset{H^+}{\rightleftharpoons}} \underset{K_1}{} \overset{+}{N}H_3 - CH_2 - COO^- \underset{(HL)}{} \overset{H^+}{\rightleftharpoons} \underset{K_2}{} NH_2 - CH_2 - COO^- \underset{(L^-)}{} \qquad (1)$$

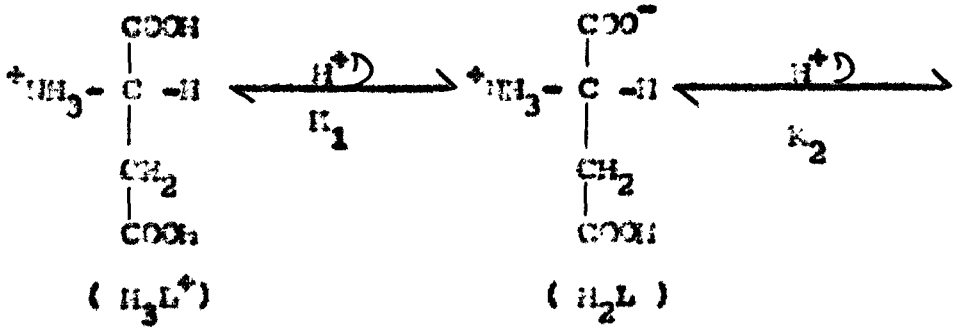
Amounts of various glycine species (as fractions of total glycine) were calculated using values of ionisation constants recorded in the Table 1 and equations 2 to 4:

$$\alpha_0 = \frac{[H_2L^+]}{\sum_{n=0}^{2} H_nL^{(n-1)+}} = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (2)$$

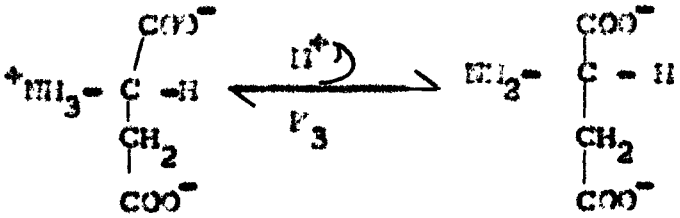
$$\alpha_1 = \frac{[HL]}{\sum_{n=0}^{2} H_nL^{(n-1)+}} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (3)$$

$$\alpha_2 = \frac{[L^-]}{\sum_{n=0}^{2} H_nL^{(n-1)+}} = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (4)$$

We have three distinct equilibria in aspartic acid which is a monoamino, dicarboxylic acid:



(H_3L^+) (H_2L)



(5)

(HL$^-$) (L^{2-})

The ammonia group does not behave much differently than the ammonia group of glycine, but the β-Carboxylic group is a weaker acid than the group on glycine and the ∝-carboxylic group is a stronger acid.

The fractions, $\alpha_0 - \alpha_3$, of aspartic acid were calculated by using the following equations:

$$\alpha_0 = \frac{[H_3L^+]}{\sum_{n=0}^{3} H_nL^{(n-2)+}} = \frac{[H^+]^3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \qquad (6)$$

$$\alpha_1 = \frac{[H_2L]}{\sum_{n=0}^{3} H_nL^{(n-2)+}} = \frac{K_1[H^+]^2}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \qquad (7)$$

$$\alpha_2 = \frac{[HL^-]}{\sum_{n=0}^{3} H_nL^{(n-2)+}} = \frac{K_1K_2[H^+]}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \qquad (8)$$

and

$$\alpha_3 = \frac{[L^{2-}]}{\sum_{n=0}^{3} H_nL^{(n-2)+}} = \frac{K_1K_2K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \qquad (9)$$

Distribution diagrams showing fractions of each ionised form at different pH are shown in Figs. 1 to 6 .

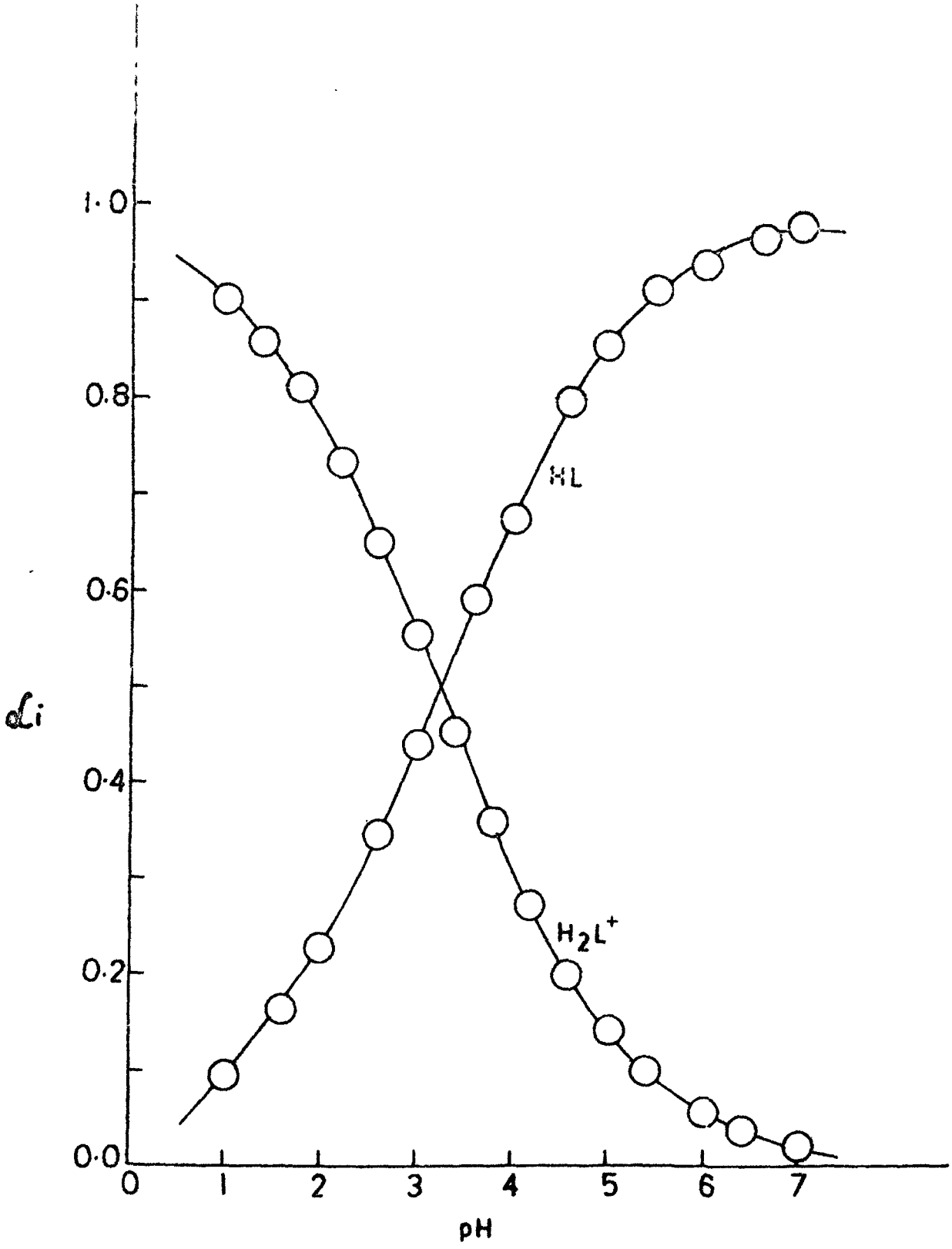


Fig. 1 : Variation with pH of the distributions (given as α_i) of several species present in aqueous solution of Glycine.

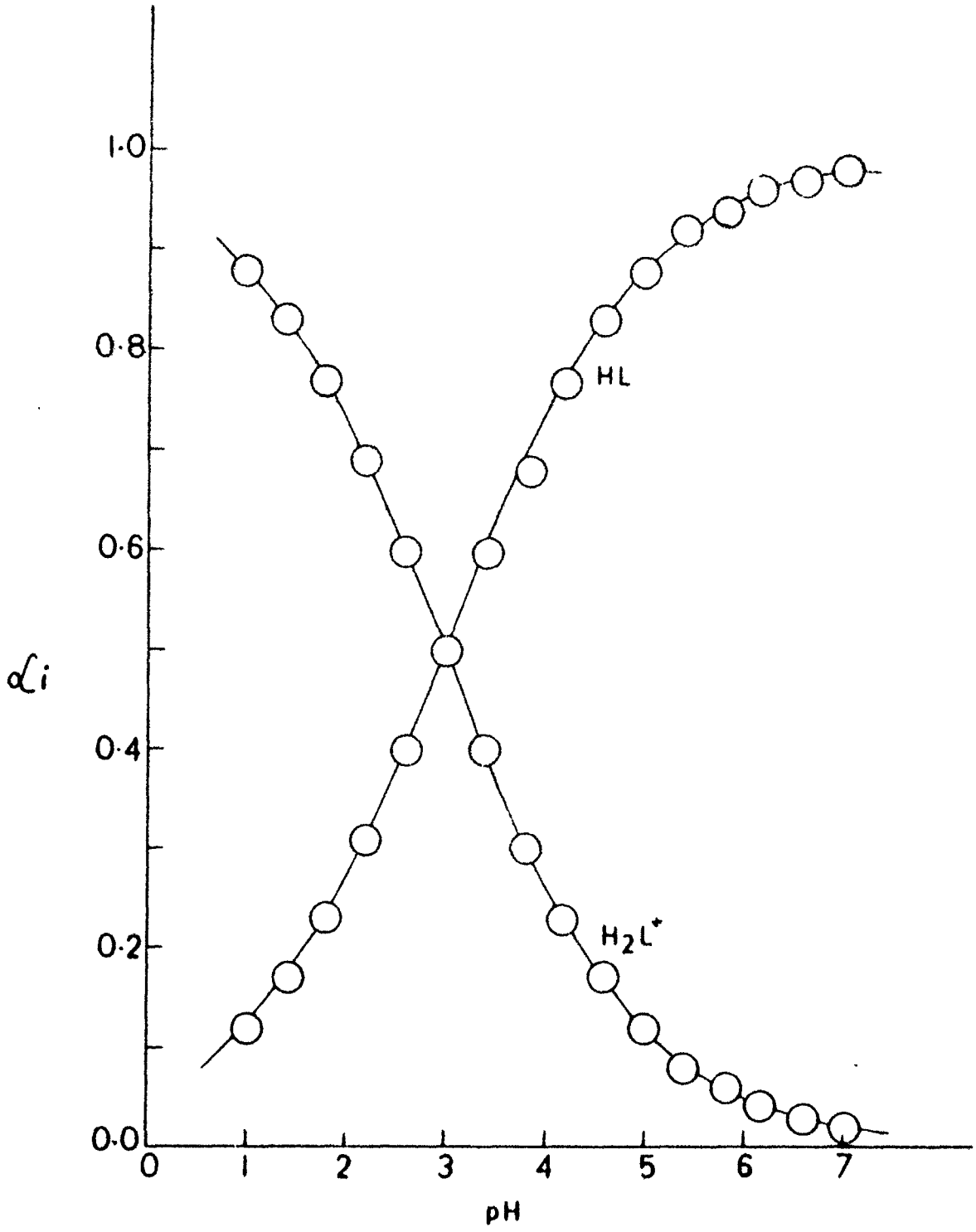


Fig. 2: Variation with pH of the distributions (given as α_i) of several species present in aqueous solution of Alanine.

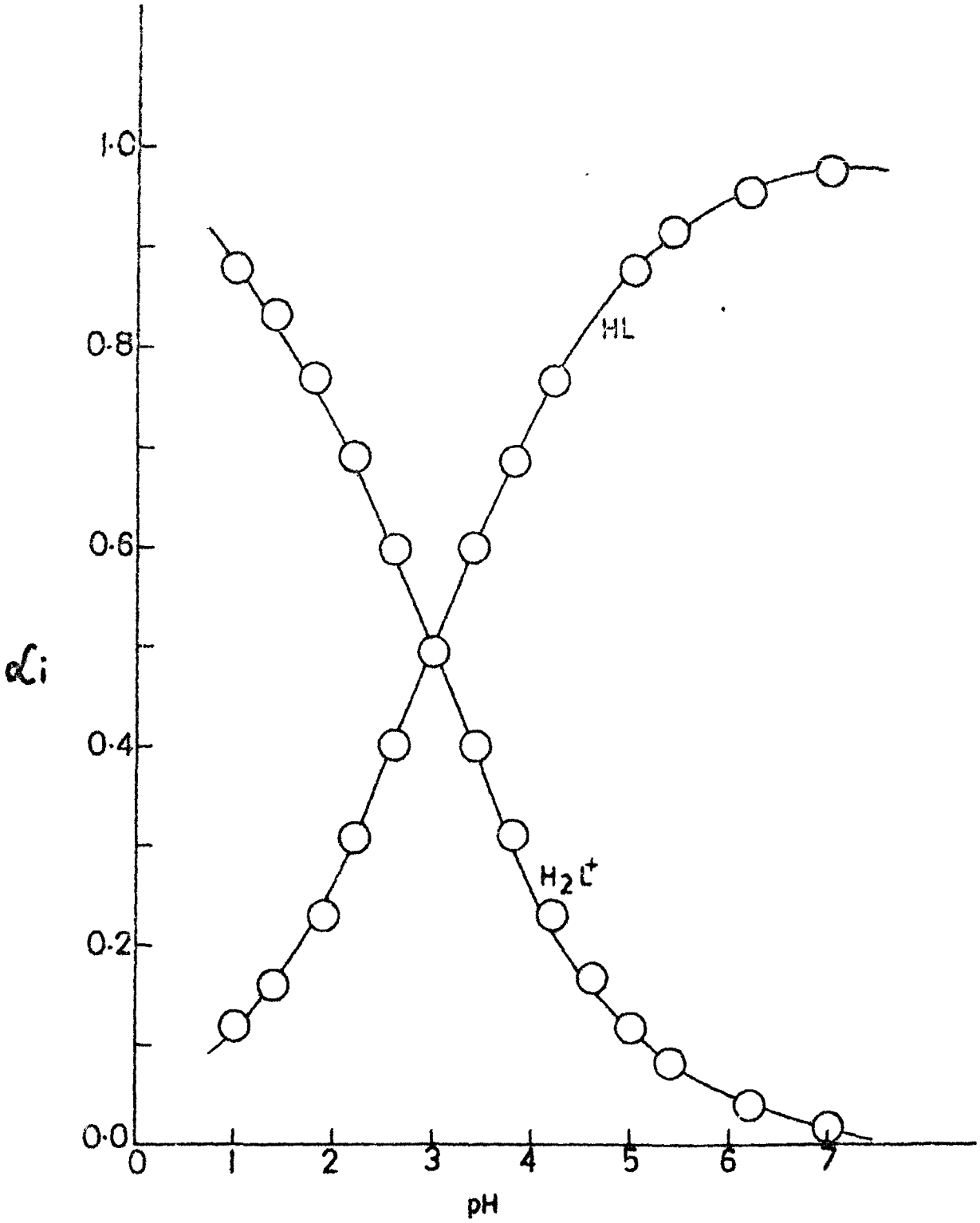


Fig. 3 : Variation with pH of the distributions (given as α_i) of several species present in aqueous solution of Valine.

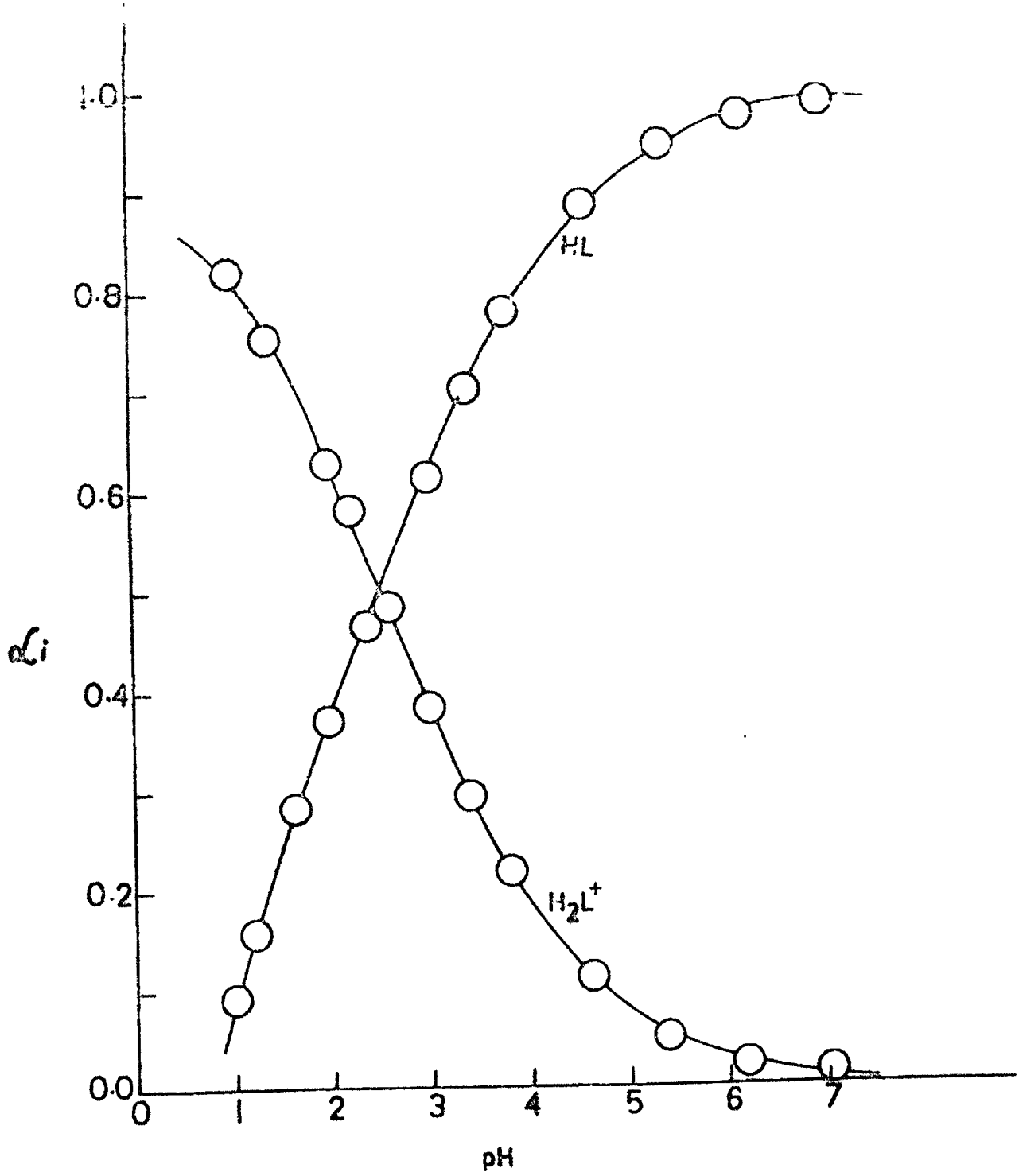


Fig. 4: Variation with pH of the distributions (given as αi) of several species present in aqueous solution of Serine.

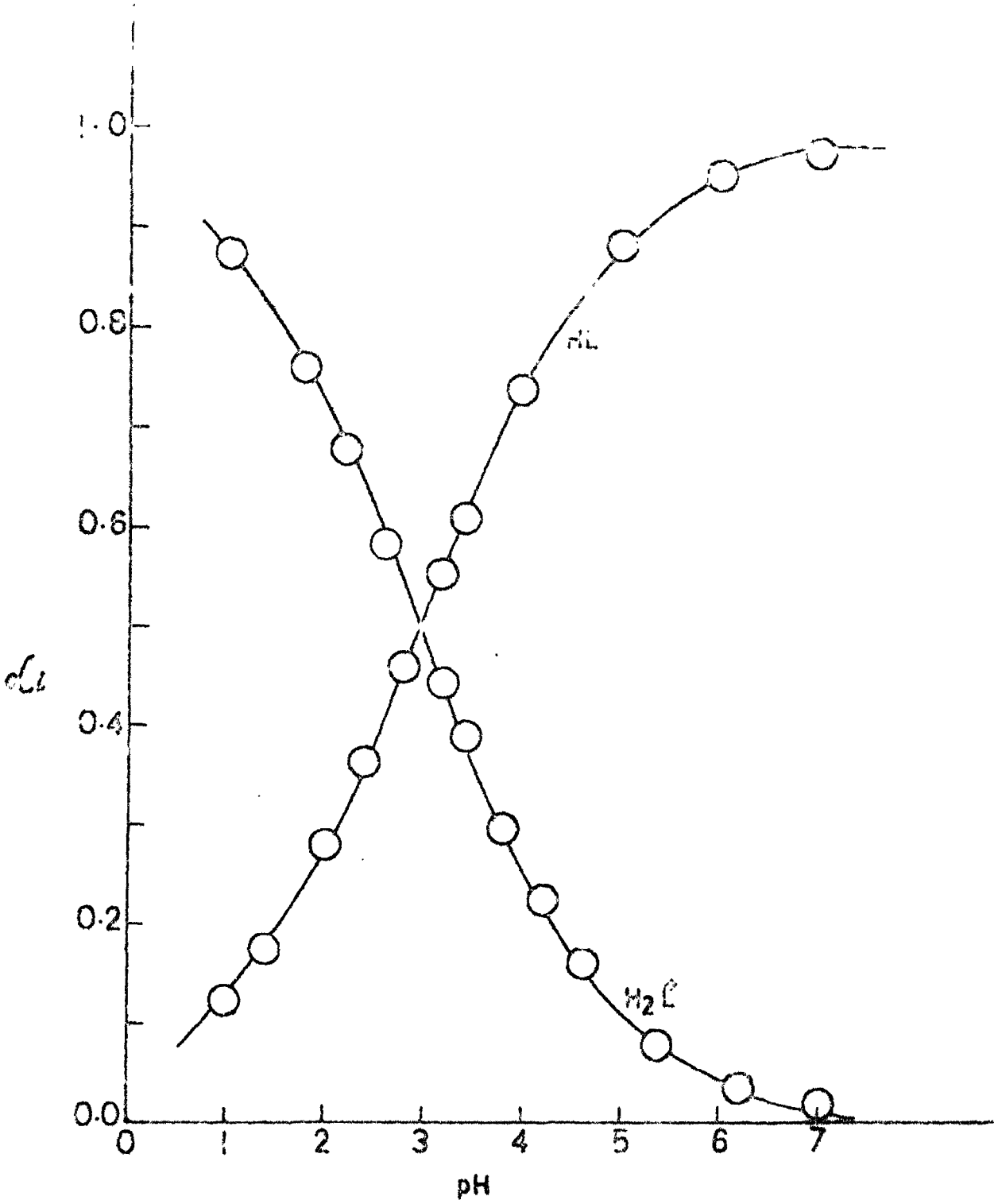


Fig.5: Variation with pH of the distributions (given as α_i) of several species present in aqueous solution of Methionine.

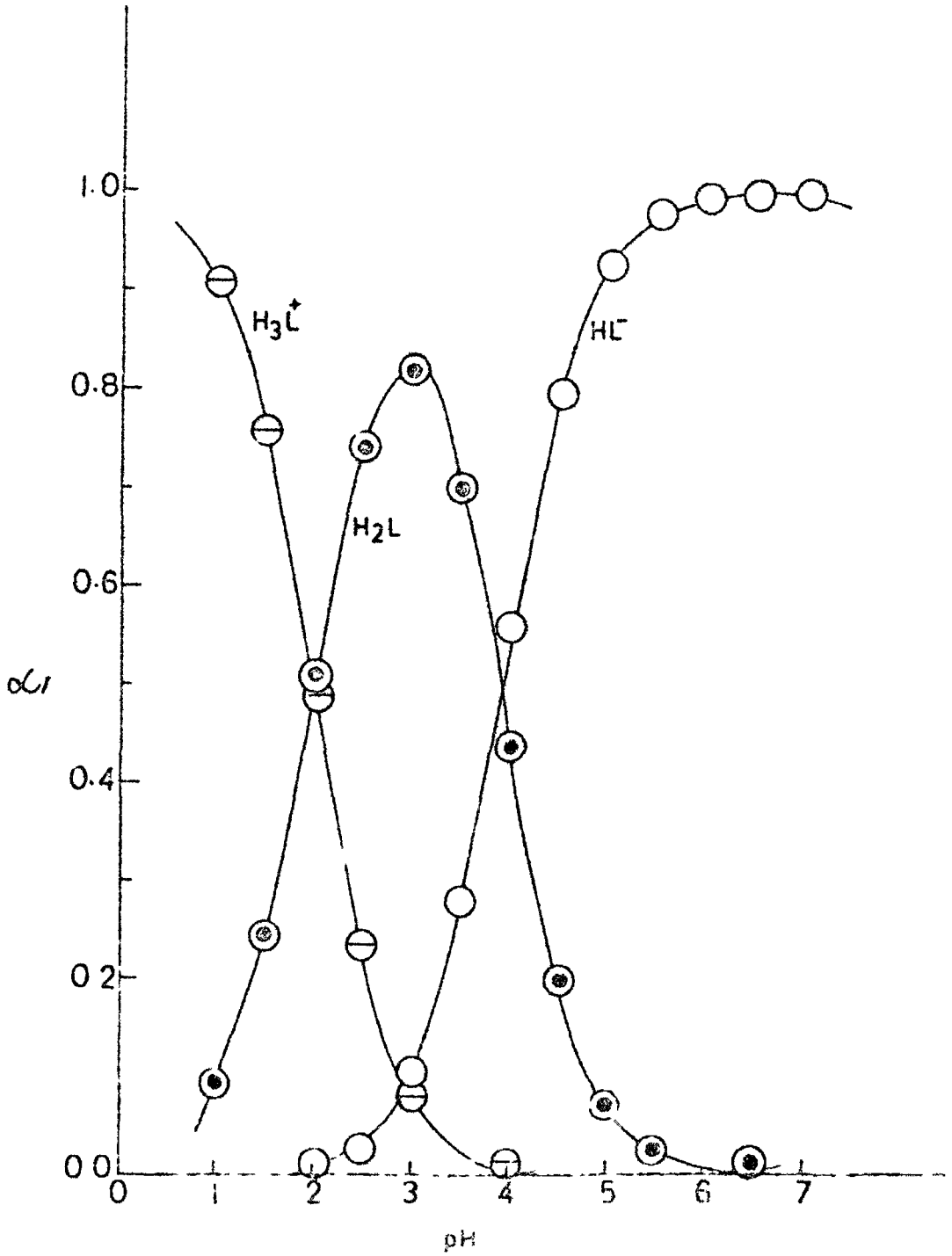


Fig. 6: Variation with pH of the distributions (given as α_i) of several species present in aqueous solution of Aspartic acid.

We see that monoamino, monocarboxylic acids exist mostly as a zwitterion over the pH-range used in the present investigations. Furthermore, the fraction of anionic form is very little (3×10^{-5} at pH = 7). In the case of aspartic acid both the zwitterion (H_2L) and anion (HL^-) exist in the range of pH used.

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CHAPTER - IV

RESULTS AND DISCUSSION

CHAPTER - IV

RESULTS AND DISCUSSION

Results of Compositions of Chromium(III)- Amino Acid Complexes.

It has been found that $Cr(H_2O)_6^{3+}$ reacts slowly with the amino acids used in the present investigation in acidic media. Colour of the complexes formed is pink-violet. Absorption spectra of solutions containing $Cr(H_2O)_6^{3+}$ and excess amino acid were recorded after boiling and keeping the solutions at 50°C for 24 h. The results represented graphically in Fig.1 2 show that maximum absorbance of all monoamino, monocarboxylic acids is at 540 nm whereas for aspartic acid the maximum absorbance occurs at 530 nm.

The wavelengths chosen for carrying out the composition studies as well as for studying the rate of the reactions of $Cr(H_2O)_6^{3+}$ with amino acids were that for maximum absorbance. $Cr(H_2O)_6^{3+}$ absorbs little at the chosen wavelengths whereas amino acids do not absorb at all.

The compositions of chromium(III)- amino acid complexes were determined by Job's method[1] of continuous variations. A series of solutions containing different metal- ligand concentrations were prepared in separate calibrated test tubes. The solutions were boiled and kept for 24h in a thermostat maintained at 50°C. Optical densities were recorded after bringing the

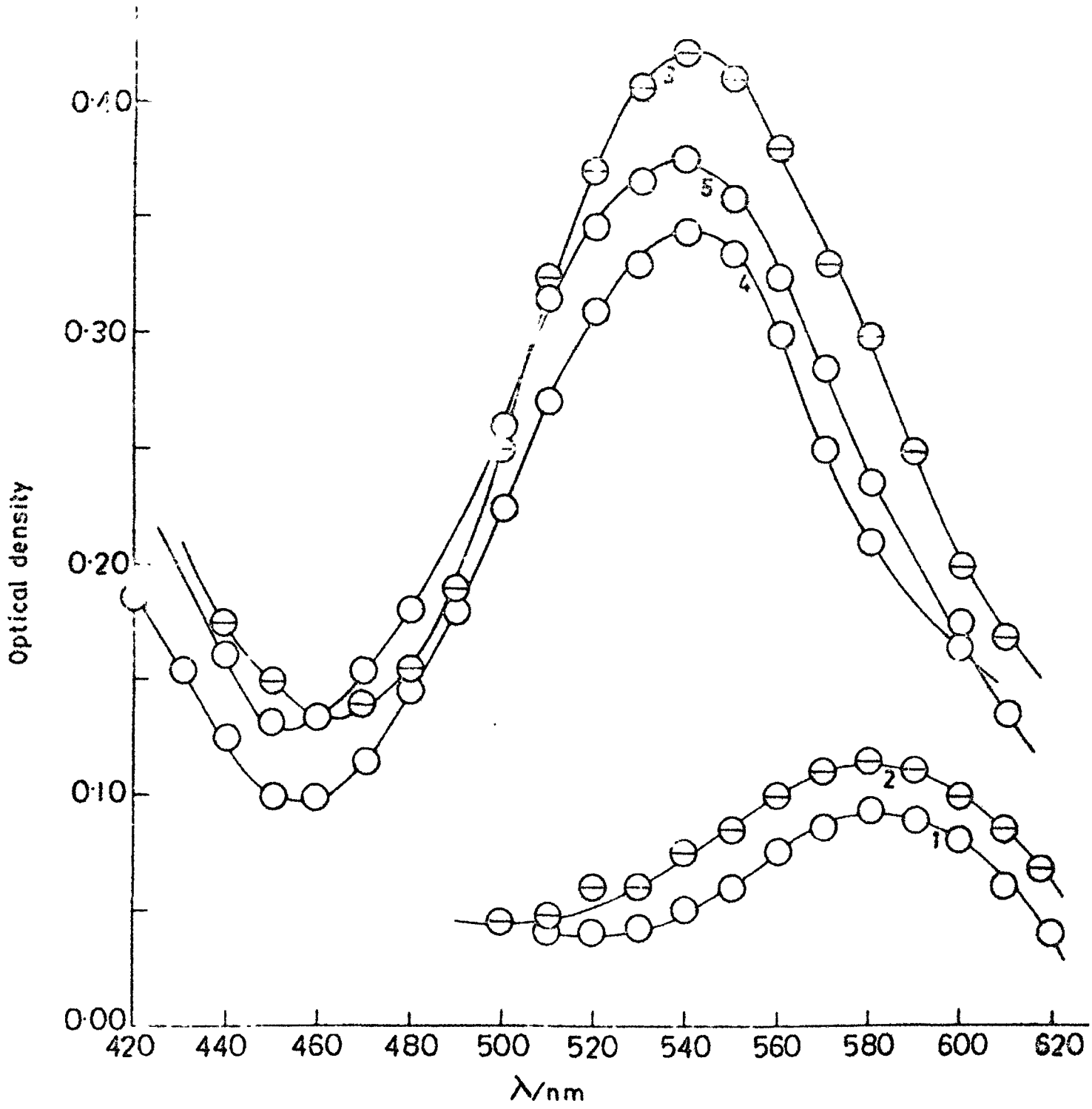

Fig.1: Spectra of metal ion and metal-amino acid complexes; (1) $[Cr(NO_3)_3] = 4 \times 10^{-3}$ M; (2) $[Cr(NO_3)_3] = 5 \times 10^{-3}$ M · Amino acids were in excess in all the solutions, (3) Chromium (III)-glycine complex, $[Cr(NO_3)_3] = 5 \times 10^{-3}$ M; (4) Chromium (III)-alanine complex, $[Cr(NO_3)_3] = 4 \times 10^{-3}$ M; (5) Chromium (III)-serine complex, $[Cr(NO_3)_3] = 4 \times 10^{-3}$ M.

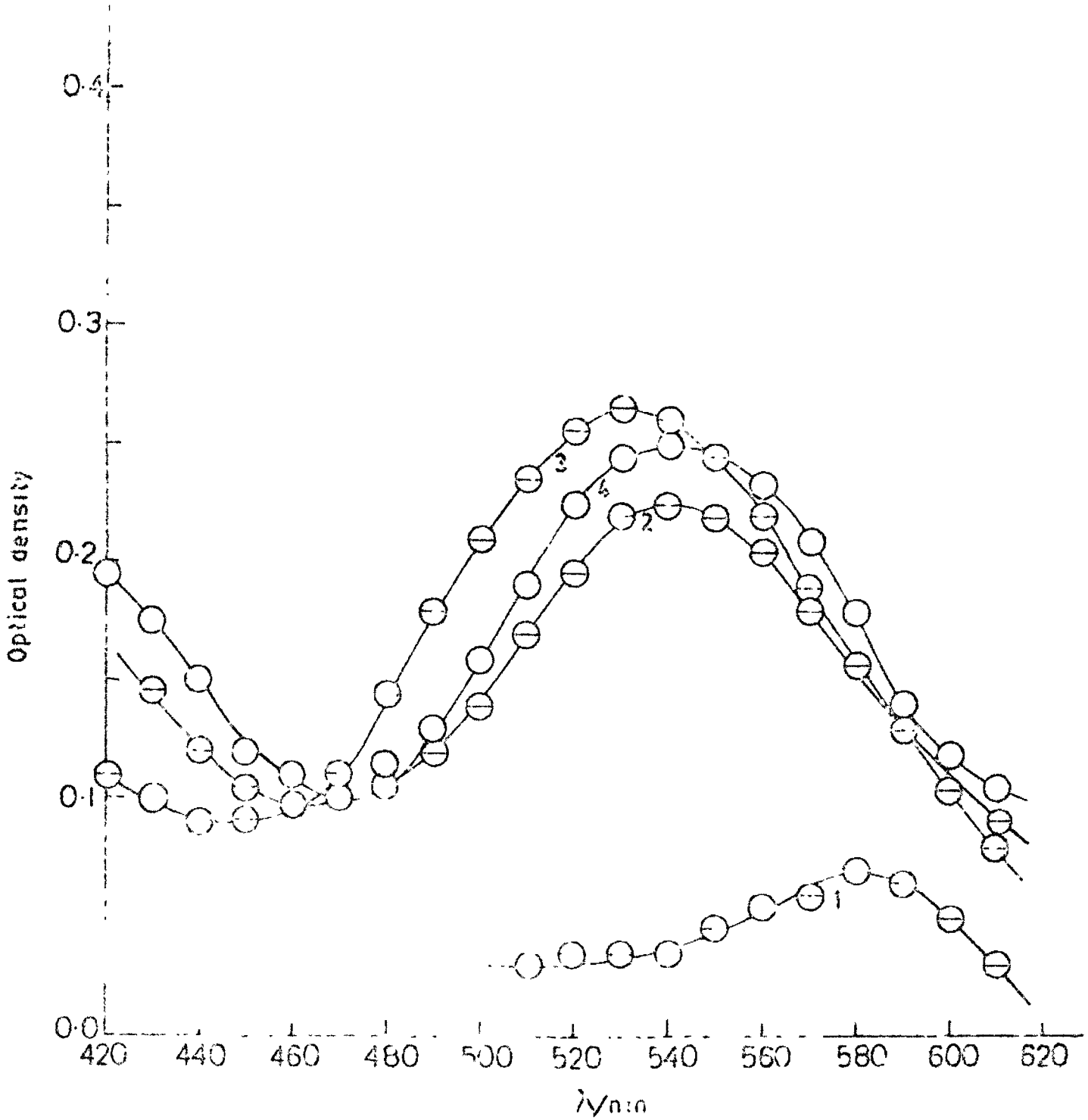

Fig. 2: Spectra of metal ion and metal amino acid complexes (1) $[Cr(NO_3)_3] = 3 \times 10^{-3}$ M. Amino acids were in excess in all the solutions, (2) Chromium-methionine complex, $[Cr(NO_3)_3] = 3 \times 10^{-3}$ M, (3) Chromium-asp. acid complex, $[Cr(NO_3)_3] = 3 \times 10^{-3}$ M, (4) Chromium-valine complex, $[Cr(NO_3)_3] = 4 \times 10^{-3}$ M.

solutions to room temperature and making upto the original volume by adding requisite amounts of water. Optical densities of solutions containing same concentrations of chromium nitrate as in the Job's solution were also recorded. The optical density difference

$$\Delta(\text{OD}) = \left[\text{OD of the complex} - \text{OD of the chromium-nitrate}\right]$$

(Tables 1-6) were plotted against mole fraction of the metal ion. Representative plots are shown in Figs.3-8 and the results are summarised in Table 7. All the results are comparable with previously published data except of Cr(III)-glycine system. Instead of frequently reported 1:3 (metal: ligand) complex formation of a 1:1 complex was observed.

Kinetic Results

The rate constants of the reaction of hexaaquochromium(III)-amino acid systems followed under varying conditions of ligand concentration, pH, ionic strength and temperature are presented for each amino acid separately in Tables 8-13.

It can be seen that the reaction rates increase with increase in concentration of the ligands, temperature, and decrease with decrease in pH. The effect of ionic strength is not well marked but a definite tendency of increase of rate constants with increase of μ was observed with all the systems (Figs. 9-14).

TABLE-1. Composition of chromium(III)-glycine complex by Job's method of continuous variations at 25°C.

Total volume=20 ml

Mole fraction of the metal ion.	[Chromium(III)]= [Glycine]$_T$= 0.01M
	$\triangle$(OD)$_{540nm}$
0.10	0.045
0.20	0.090
0.30	0.110
0.40	0.135
0.50	0.155
0.60	0.150
0.70	0.120
0.80	0.100
0.90	0.070
1.00	0.000

Fig.3

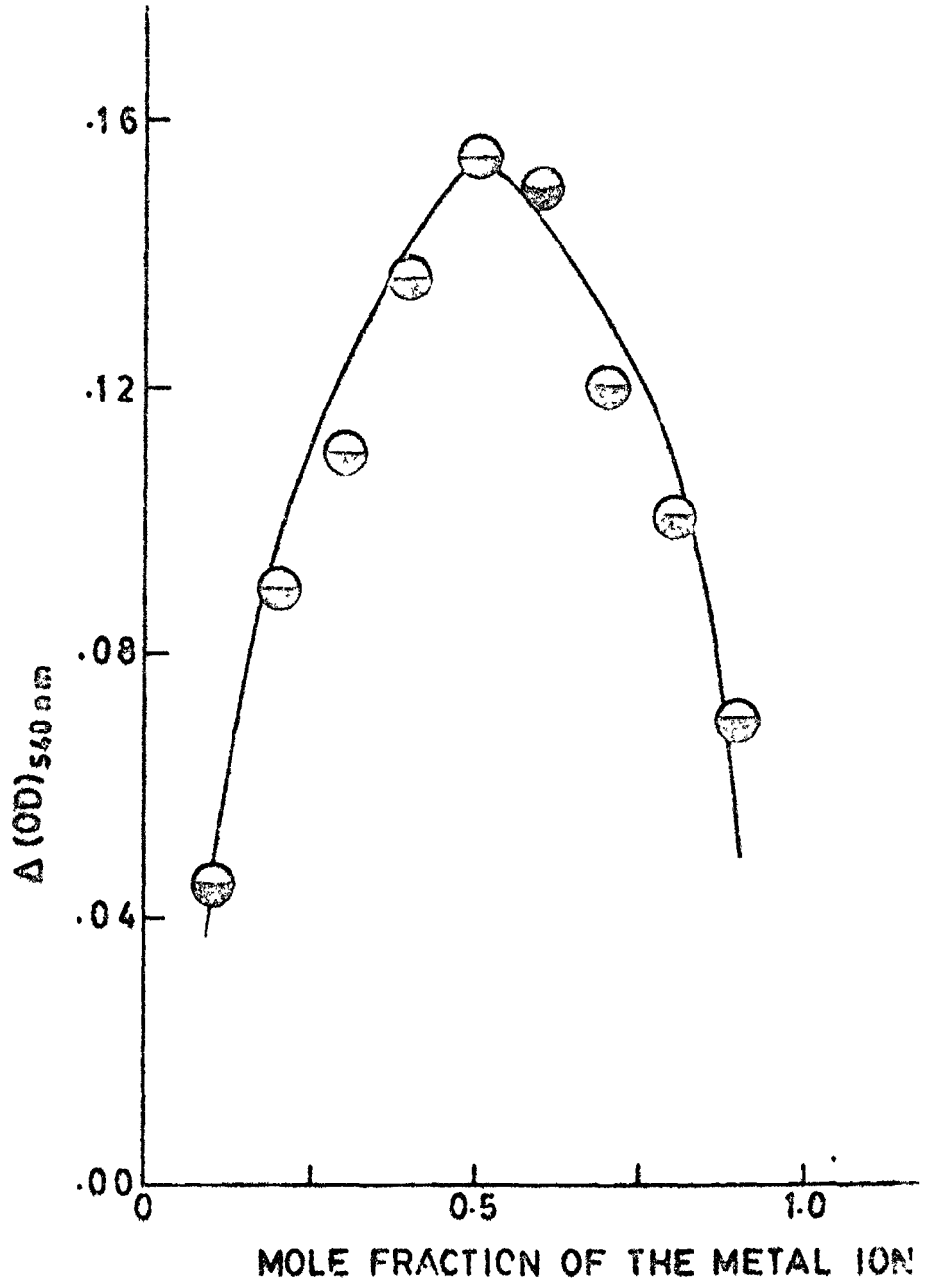

Fig. 3· Job's plot for Cr(III)–glycine complex; $[Cr^{3+}] = [glycine]_T = 0{\cdot}01\ M$.

TABLE-2. Composition of chromium(III)-alanine complex by Job's method of continuous variations at 25°C.

[Chromium(III)] = b

$[Alanine]_T$ = b

Total volume = 20 ml

Mole fraction of the metal ion	b = 0.006M	b = 0.01M
	$\triangle (OD)_{540nm}$	$\triangle (OD)_{540nm}$
0.1	0.025	0.050
0.2	0.45	0.075
0.3	0.050	0.075
0.4	0.050	0.070
0.5	0.045	0.060
0.6	0.040	0.055
0.7	0.035	0.050
0.8	0.025	0.035
0.9	0.015	0.020
1.0	0.000	0.000

Fig.4

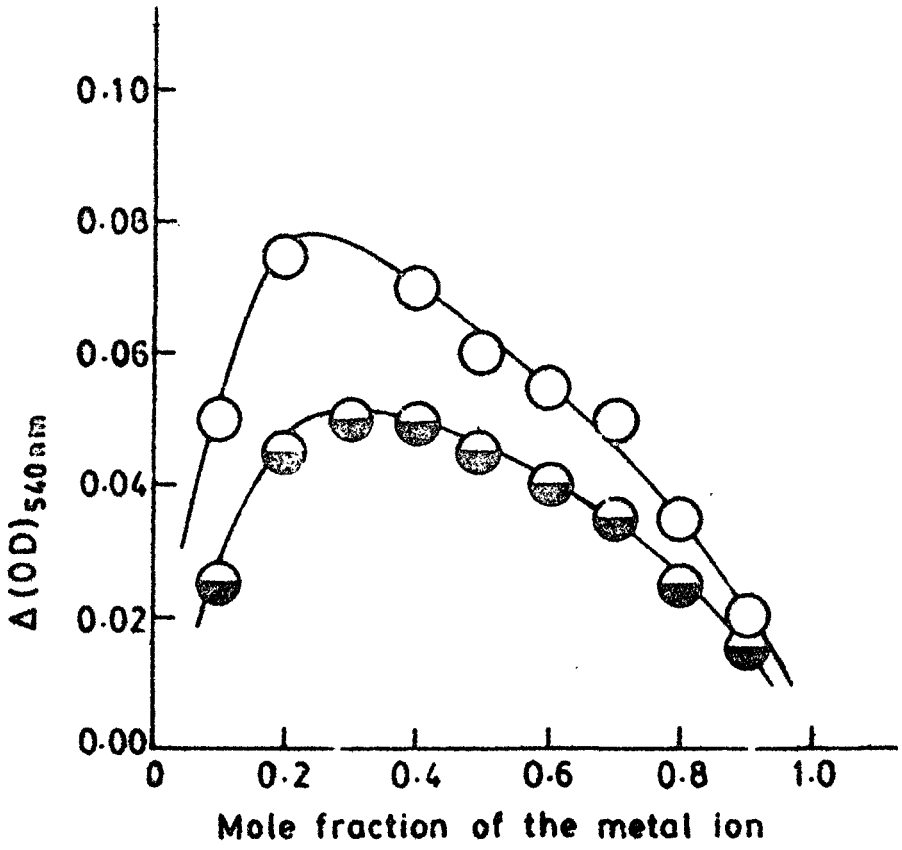

Fig.4: Job's plot for Cr(III) alanine complex; $[Cr^{3+}] = [Alanine]_T = 0{\cdot}006\,M$-◒, $0{\cdot}01\,M$-○.

TABLE-3. Complex of chromium(III)-DL-valine complex by Job's method of continuous variations at 25°C.

[Chromium(III)] = b

$[Valine]_T$ = b

Total volume = 20 ml

Mole fraction of the metal ion.	b = 0.01M	b = 0.02M
	$\triangle (OD)_{540nm}$	$\triangle (OD)_{540nm}$
0.10	0.025	0.055
0.20	0.040	0.075
0.30	0.045	0.080
0.40	0.040	0.075
0.50	0.035	0.070
0.60	0.030	0.060
0.70	0.030	0.050
0.80	0.020	0.040
0.90	0.010	0.020
1.00	0.000	0.000

Fig.5

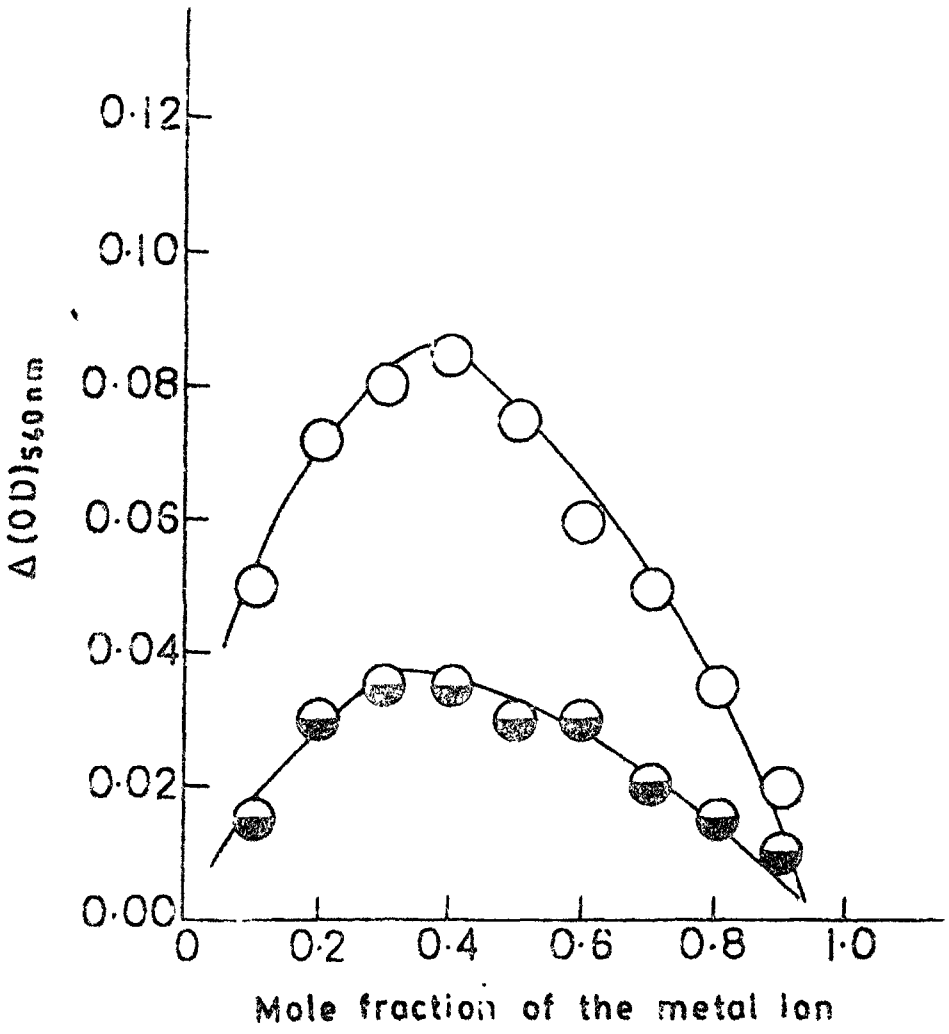

Fig.5: Job's plot for Cr(III)–valine complex; $[Cr^{3+}] = [Valine]_T = 0{\cdot}01\,M$–◒ $0{\cdot}02\,M$–◯

TABLE-4. Composition of chromium(III)-L-serine complex by Job's method of continuous variations at 25°C.

[Chromium(III)] = b

$[Serine]_T$ = b

Total volume = 20 ml

Mole fraction of the metal ion.	b = 0.01M	b = 0.02M
	$\triangle (OD)_{540nm}$	$\triangle (OD)_{540nm}$
0.10	0.025	0.0450
0.20	0.035	0.065
0.30	0.045	0.075
0.40	0.040	0.070
0.50	0.035	0.065
0.60	0.030	0.055
0.70	0.025	0.045
0.80	0.015	0.040
0.90	0.010	0.020
1.00	0.000	0.000

Fig.6

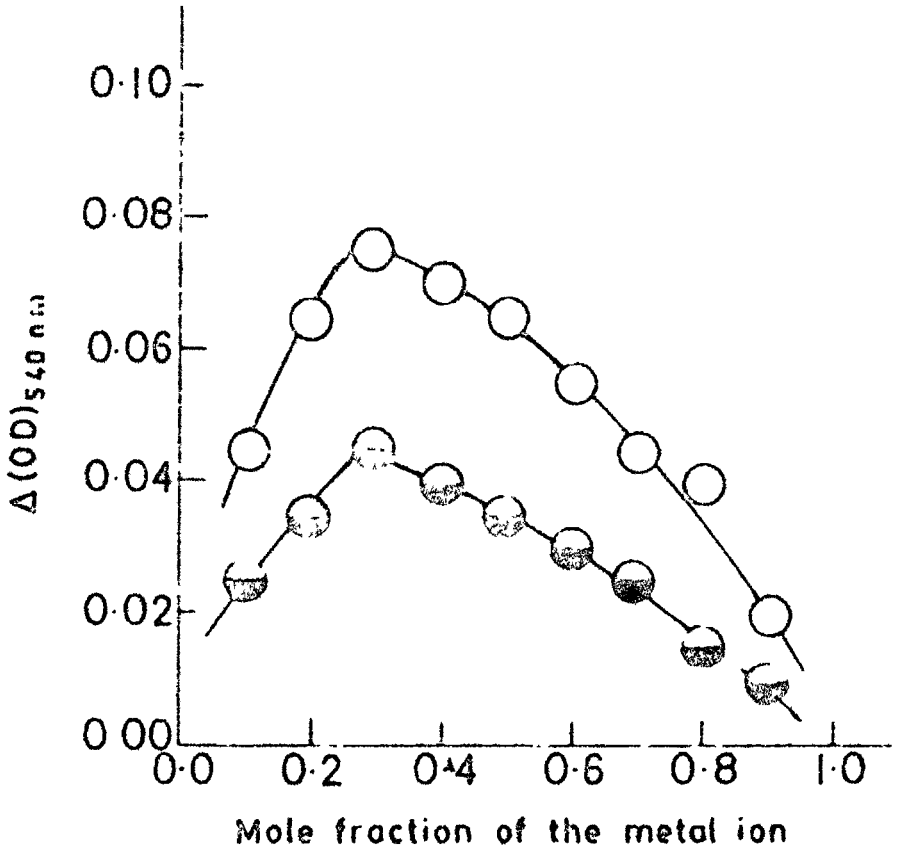

Fig.6: Job's plot Cr(III)–serine complex;
$[Cr^{3+}] = [Serine]_T = 0{\cdot}01$ M—◒, 0 02M–○.

TABLE-5. Composition of chromium(III)-DL-methionine complex by Job's method of continuous variations at 25°C.

[Chromium(III)] = b

$[Methionine]_T$ = b

Total volume = 20 ml

Mole fraction of the metal ion.	b = 0.01M	b =0.02M
	$\triangle(OD)_{540nm}$	$\triangle(OD)_{540nm}$
0.10	0.030	0.065
0.20	0.045	0.090
0.30	0.065	0.105
0.40	0.065	0.100
0.50	0.055	0.090
0.60	0.050	0.070
0.70	0.035	0.060
0.80	0.020	0.045
0.90	0.015	0.025
1.00	0.000	0.000

Fig.7

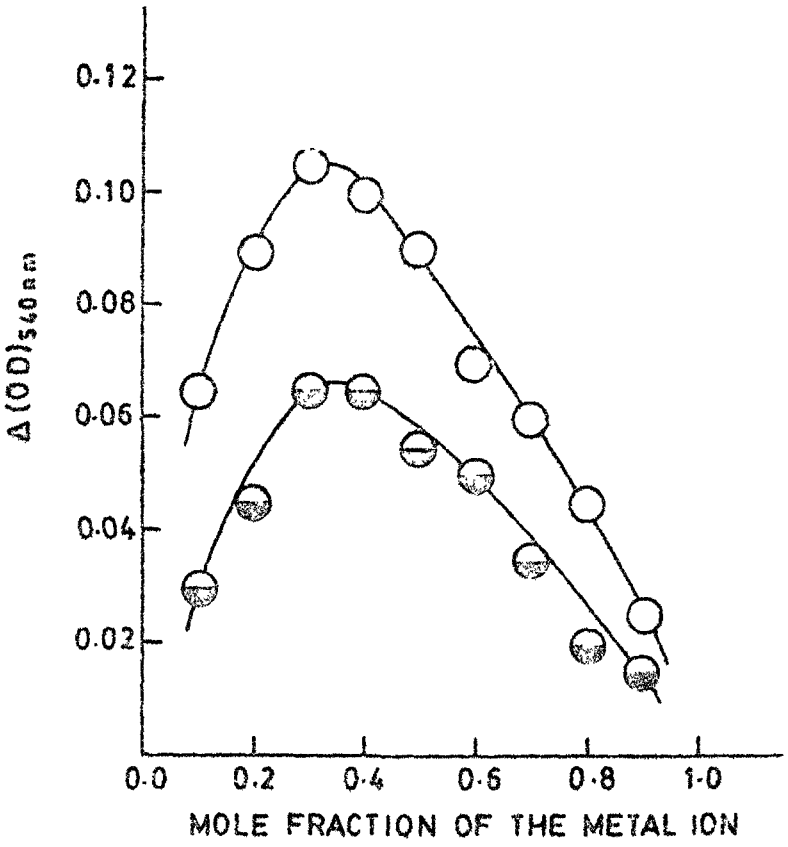

Fig. 7: Job's plot for Cr(III)-methionine complex; $[Cr^{3+}] = [\text{methionine}]_T = 0.01\,M$—◉, $0.02\,M$—○.

TABLE-6. Composition of chromium(III)-DL-aspartic acid complex by Job's method of continuous variations at 25°C.

[Chromium(III)] = b

$[Aspartic\ acid]_T$ = b

Total volume = 10 ml

Mole fraction of the metal ion.	b = 0.01M	b = 0.02M
	$\triangle(OD)_{530nm}$	$\triangle(OD)_{530nm}$
0.10	0.050	0.115
0.20	0.070	0.275
0.30	0.080	0.310
0.40	0.090	0.320
0.50	0.095	0.320
0.60	0.085	0.265
0.70	0.075	0.185
0.80	0.055	0.110
0.90	0.040	0.050
1.00	0.000	0.000

Fig.8

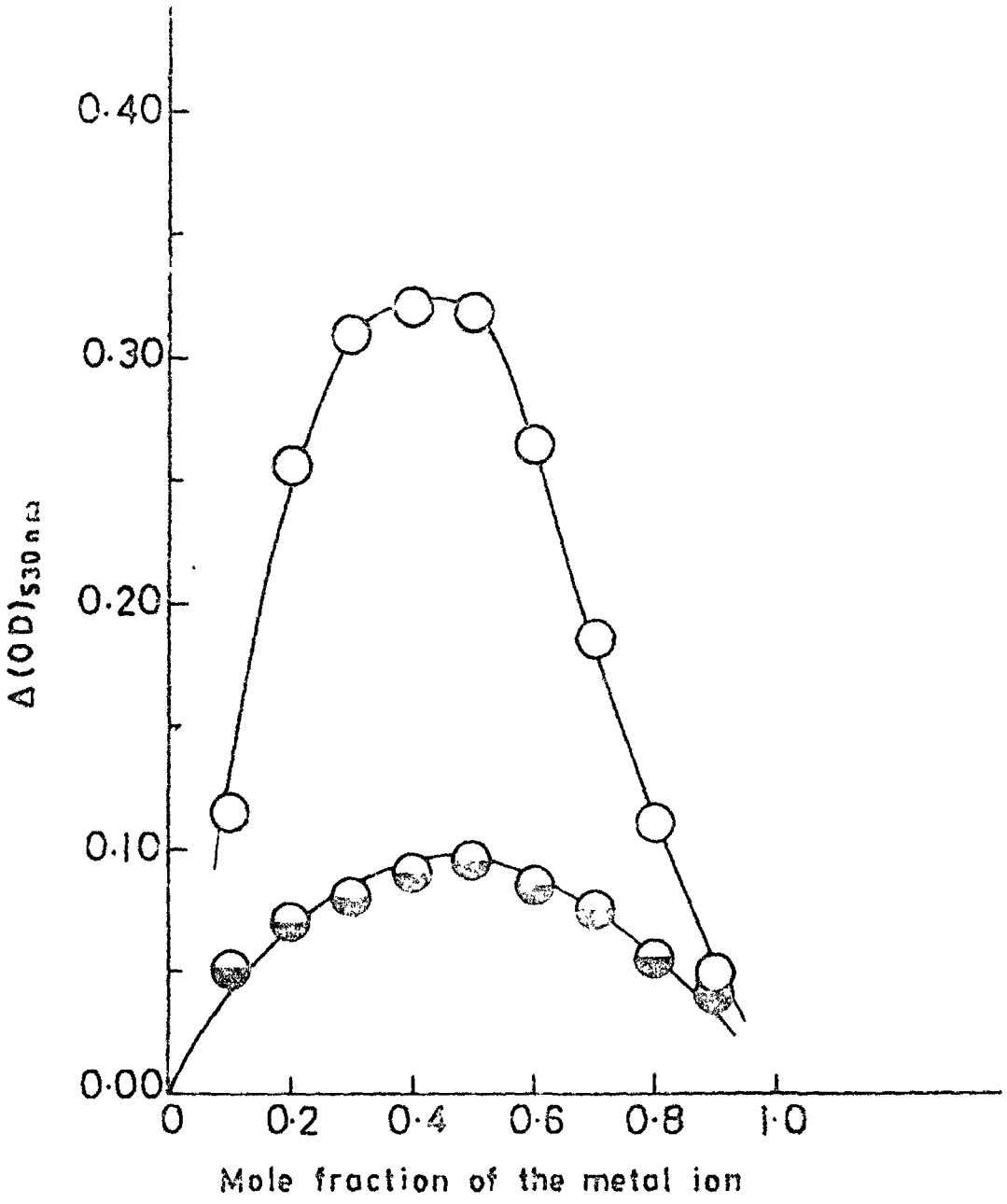

Fig. 8: Job's plot for Cr(III)–aspartic acid complex; $[Cr^{3+}] = [\text{Aspartic acid}]_T = 0.01M$ —◒, 0·02 M—◯.

TABLE-7. Summary of the results of Job's method.

Complex	Composition	Literature data
Cr(III)-glycine	1:1	(1:3)[a,d]
Cr(III)-alanine	1:3	(1:3)[a,b,c]
Cr(III)-valine	1:2	(1:2)[d]
Cr(III)-serine	1:3	(1:3)[c]
Cr(III)-methionine	1:2	(1:2)[e]
Cr(III)-aspartic acid	1:1	(1:1)[e,f,g]

[a] H.Oki and K. Otsuka, Bull.Chem.Soc.Jpn.42(7)(1976)1841.

[b] R.W.Green and K.P.Ang, J.Am.Chem.Soc.,77(1955)5482.

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TABLE-8. Summary of the values of rate constants (k_{obs}) for the anation of chromium(III) with glycine.

Temp. (°C)	μ (M)	$10^3[Cr^{3+}]$ (M)	$10^4[H^+]$ (M)	10^3 k_{obs} (min^{-1})			
				$[Glycine]_T$ (M)			
				0.05	0.10	0.20	0.30
45	1.0	5.0	3.981	1.70	3.21	6.02	8.33
45	1.0	5.0	1.259	2.22	4.16	7.69	11.10
45	1.0	5.0	0.316	3.12	6.25	10.00	14.28
50	1.0	5.0	3.981	2.70	5.00	10.00	11.25
50	1.0	5.0	1.259	3.03	5.82	10.98	14.49
50	0.8	5.0	1.259		5.78		
50	0.6	5.0	1.259		5.75		
50	0.4	5.0	1.259		5.75		
50	0.2	5.0	1.259		5.73		
50	0.1	5.0	1.259		5.72		
55	1.0	5.0	3.981	3.57	7.69	13.33	19.23
55	1.0	5.0	1.259	6.21	11.52	22.77	26.31

TABLE-9. Summary of the values of rate constants (k_{obs}) for the anation of chromium(III) with DL-α-alanine.

Temp. (°C)	μ (M)	10^3[Cr^{3+}] (M)	10^4[H^+] (M)	10^3 k_{obs} (min^{-1})					
				[Alanine]$_T$ (M)					
				0.040	0.080	0.100	0.125	0.160	0.220
45	1.00	4.0	5.012	0.93	1.63	1.82	2.34	2.76	3.57
45	1.00	4.0	1.581	1.56	2.85	3.20	3.45	4.27	6.18
45	1.00	4.0	0.398	3.84	5.00	5.88	5.88	7.41	8.36
50	1.00	4.0	5.012	1.12	1.98	2.60	2.85	3.74	5.15
50	1.00	4.0	1.581	2.70	4.76	5.20	5.71	6.89	9.08
50	0.80	4.0	1.581	2.70					
50	0.60	4.0	1.581	2.69					
50	0.40	4.0	1.581	2.68					
50	0.20	4.0	1.581	2.69					
55	1.00	4.0	5.012	1.66	3.05	3.92	4.54	5.88	7.04
55	1.00	4.0	1.581	5.14	7.58	9.14	10.53	12.50	16.65

TABLE-10. Summary of the values of rate constants (k_{obs}) for the anation of chromium(III) with DL- valine.

Temp. (°C)	μ (M)	$10^3[Cr^{3+}]$ (M)	$10^4[H^+]$ (M)	$10^3 k_{obs}$ (min^{-1})						
				$[Valine]_T$ (M)						
				0.04	0.6	0.08	0.10	0.12	0.16	0.20
35	1.00	4.0	2.512	1.60	2.19	2.98	3.33	4.00	4.54	5.72
35	1.00	4.0	1.585	2.50	3.38	4.08	4.65	5.71	6.66	7.18
40	1.00	4.0	3.981	3.27	4.54	5.38	6.85	7.86	9.92	11.12
40	1.00	4.0	2.518	4.50	6.02	7.46	8.92	9.44	12.04	13.88
40	1.00	4.0	1.585	5.61	7.57	9.60	11.36	11.62	14.28	15.38
45	1.00	4.0	3.981	7.69	10.75	12.20	14.28	17.24	19.23	23.23
45	0.80	4.0	3.981			12.08				
45	0.60	4.0	3.981			12.09				
45	0.40	4.0	3.981			12.06				
45	0.20	4.0	3.981			12.08				
45	1.00	4.0	2.518	10.20	12.82	16.12	17.86	20.83	25.00	26.31
45	1.00	4.0	1.585	13.81	18.52	20.41	21.74	23.81	29.41	32.26

TABLE-11. Summary of the values of rate constants (k_{obs}) for the anation of chromium(III) with DL-serine.

Temp. (°C)	μ (M)	$10^3[Cr^{3+}]$ (M)	$10^4[H^+]$ (M)	10^2 k_{obs} (min^{-1})					
				$[Serine]_T$ (M)					
				0.04	0.07	0.10	0.13	0.16	0.22
45	1.00	4.0	12.590	0.11	0.18	0.26	0.29	0.34	0.43
45	1.00	4.0	4.467	0.22	0.34	0.42	0.48	0.58	0.65
45	1.00	4.0	1.413	0.38	0.51	0.58	0.67	0.69	0.83
45	0.80	4.0	1.413						0.83
45	0.60	4.0	1.413						0.82
45	0.40	4.0	1.413						0.82
45	0.20	4.0	1.413						0.78
50	1.00	4.0	12.595	0.19	0.31	0.38	0.50	0.54	0.71
50	1.00	4.0	4.476	0.35	0.53	0.66	0.75	0.83	1.00
50	1.00	4.0	1.413	0.91	1.11	1.25	1.28	1.32	1.54
54	1.00	4.0	12.590	0.30	0.48	0.71	0.80	0.86	1.17
55	1.00	4.0	4.467	0.65	0.95	1.08	1.25	1.54	2.00

TABLE-12. Summary of the values of rate constants (k_{obs}) for the anation of chromium(III) with DL- methionine.

Temp. (°C)	μ (M)	$10^3[Cr^{3+}]$ (M)	$10^4[H^+]$ (M)	$10^3\ k_{obs}$ (min^{-1})				
				$[Methionine]_T$ (M)				
				0.03	0.06	0.09	0.12	0.15
35	1.00	3.0	1.585	1.02	1.92	2.78	3.38	3.78
35	1.00	3.0	0.635	1.85	3.22	4.41	5.40	6.25
40	1.00	3.0	3.981	1.15	2.15	2.94	3.76	4.65
40	1.00	3.0	1.585	1.88	3.27	4.65	5.88	6.45
40	1.00	3.0	0.635	3.80	6.45	8.32	10.00	11.10
40	0.80	3.0	0.635	3.75				
40	0.60	3.0	0.635	3.72				
40	0.40	3.0	0.635	3.66				
40	0.20	3.0	0.635	3.64				
45	1.00	3.0	3.981	1.90	3.50	4.85	5.86	7.69
45	1.00	3.0	1.585	3.44	6.25	9.50	10.50	11.76
45	1.00	3.0	0.635	7.14	12.50	15.54	18.18	21.05

TABLE-13. Summary of the values of rate constants (k_{obs}) for the anation of chromium(III) with DL- aspartic acid.

Temp. (°C)	μ (M)	$10^3[Cr^{3+}]$ (M)	$10^4[H^+]$ (M)	10^3 k_{obs} (min^{-1})				
				$[Aspartic\ acid]_T$ (M)				
				0.03	0.06	0.09	0.12	0.15
35	1.0	3.0	10.000	1.92	3.00	3.67	4.00	4.50
35	1.0	3.0	3.162	2.05	3.27	3.88	4.44	4.70
35	1.0	3.0	1.000	2.17	3.42	4.25	4.94	5.19
40	1.0	3.0	10.000	3.05	4.54	5.71	6.25	6.89
40	1.0	3.0	3.162	3.45	5.47	6.45	7.27	8.33
40	1.0	3.0	1.000	3.80	5.98	7.58	8.16	9.08
45	1.0	3.0	10.000	5.33	7.84	10.00	10.52	11.76
45	1.0	3.0	3.162	6.25	9.09	11.12	12.50	14.28
45	1.0	3.0	1.000	7.40	11.12	12.90	15.38	17.39
45	0.7	3.0	1.000		11.03			
45	0.5	3.0	1.000		10.98			
45	0.3	3.0	1.000		10.89			
45	0.1	3.0	1.000		10.815			

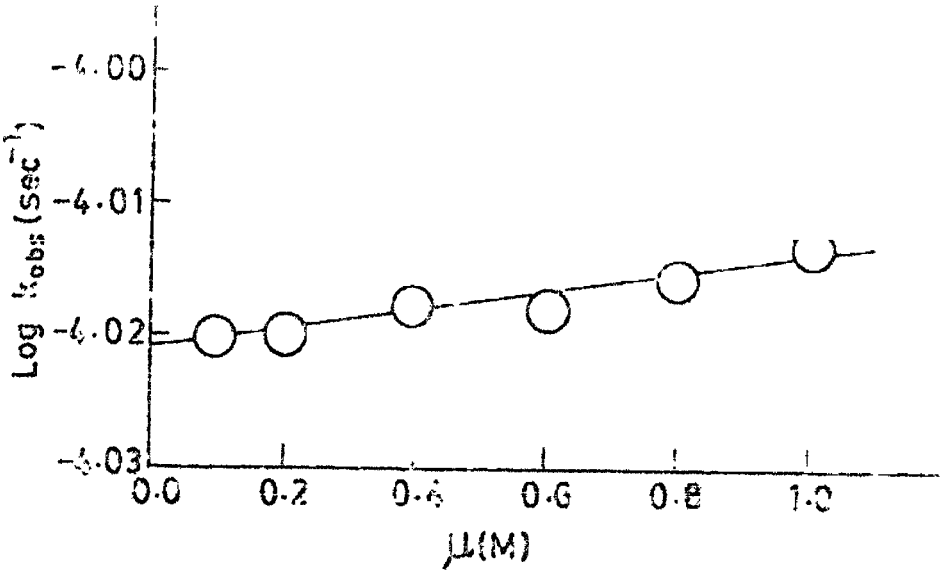


Fig.9: Dependence of rate constant (k_{obs}) on ionic strength (μ) at 50 °C; $[Cr^{3+}] = 3 \times 10^{-3}$ M, $[Glycine]_T = 0.1$ M, $[H^+] = 1.259 \times 10^{-5}$ M.

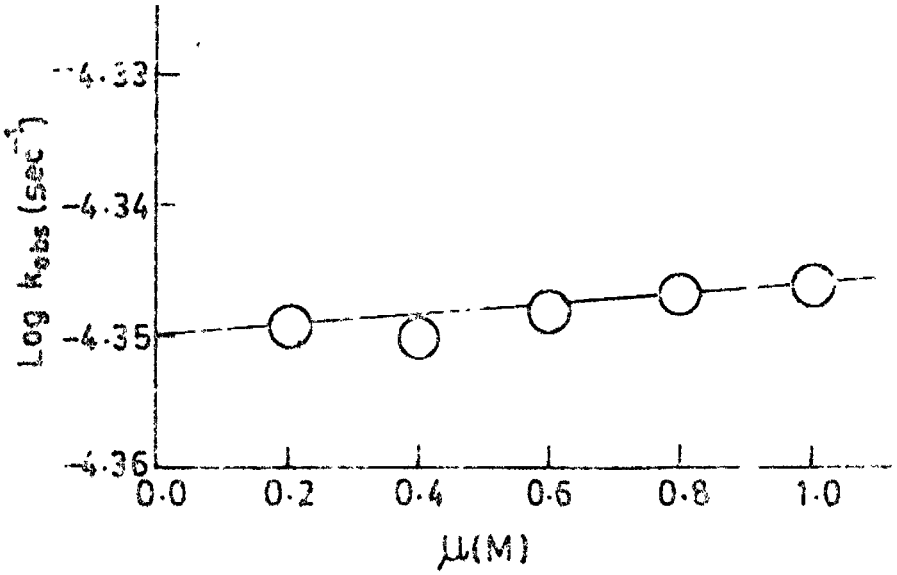


Fig.10: Dependence of rate constant (k_{obs}) on ionic strength at 50 °C; $[Cr^{3+}] = 4 \times 10^{-3}$ M, $[Alanine]_T = 0.04$ M, $[H^+] = 1.581 \times 10^{-4}$ M.

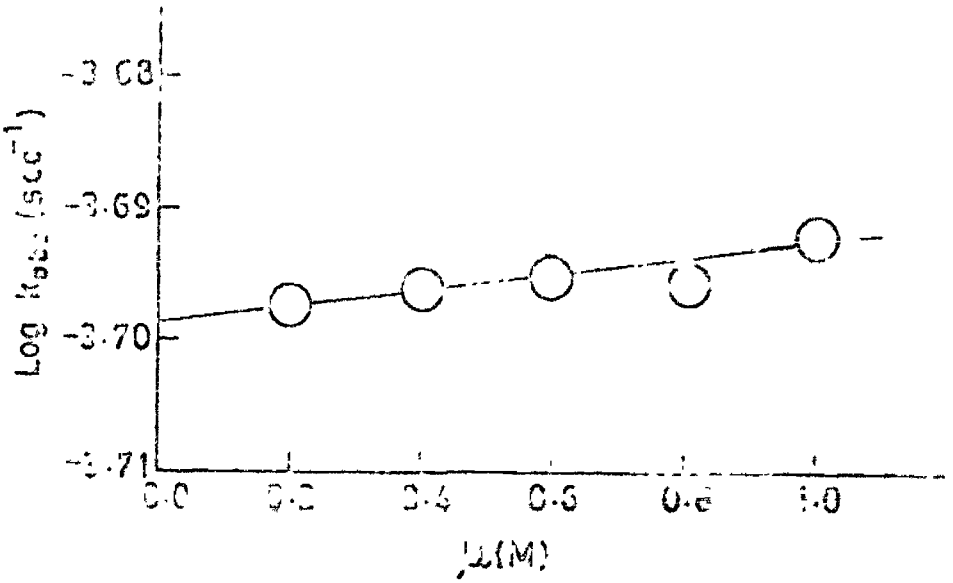


Fig.11 : Dependence of rate constant (k_{obs}) on ionic strength (μ) at 40 °C; $[Cr^{3+}]$ = 4 × 10^{-3} M, [Serine]$_T$ = 0·08 M, $[H^+]$ = 1·535 × 10^{-4} M.

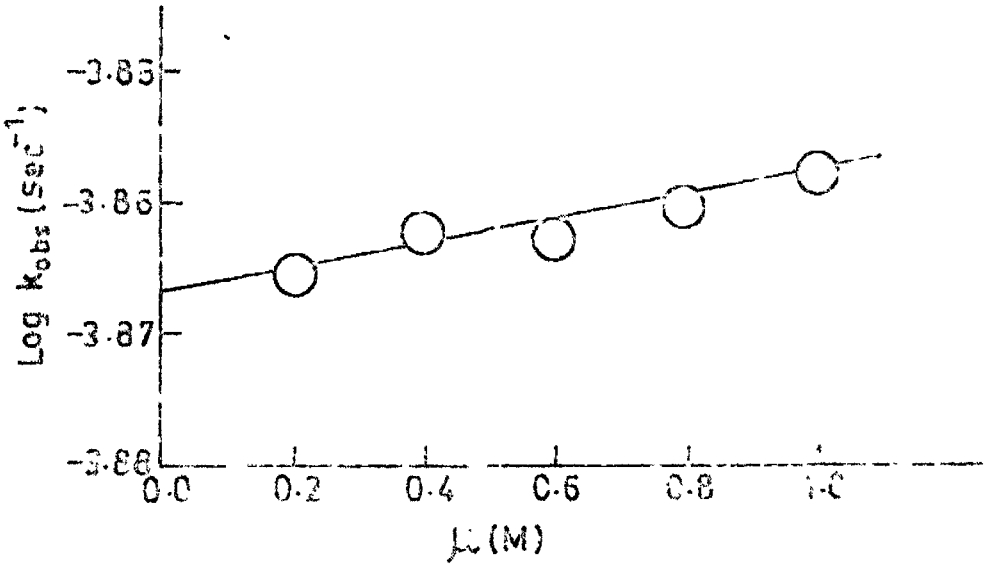


Fig.12: Dependence of rate constant (k_{obs}) on ionic strength (μ) at 45 °C; $[Cr^{3+}]$ = 4 × 10^{-3} M, [Serine]$_T$ = 0·22 M, $[H^+]$ = 1·413 × 10^{-4} M.

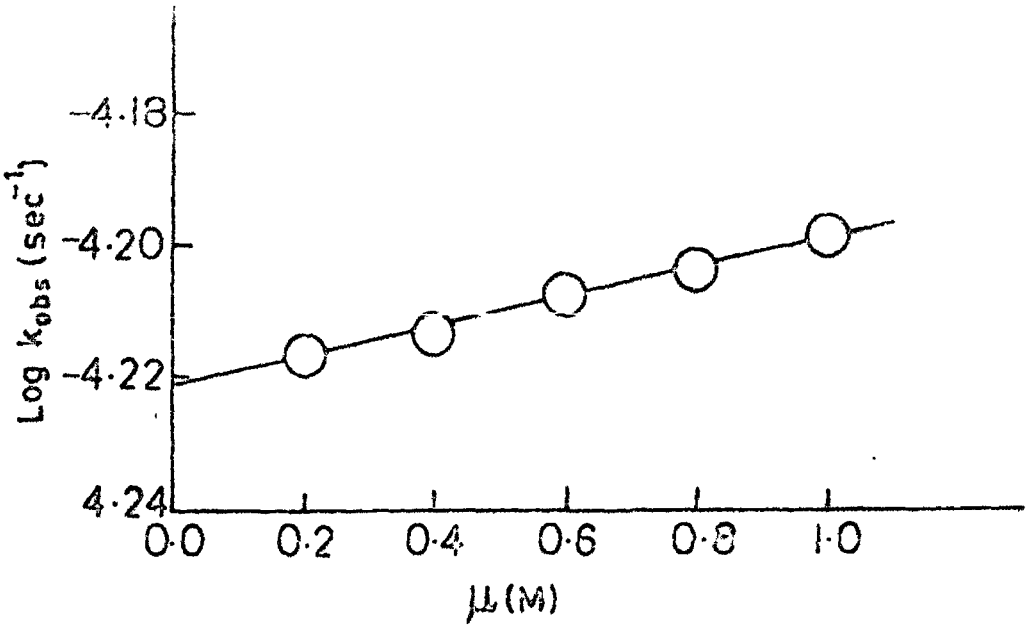


Fig.13: Dependence of rate constant (k_{obs}) on ionic strength (μ) at 40 °C; $[Cr^{3+}] = 3 \times 10^{-3}$ M, $[Methionine]_T = 0.03$ M; $[H^+] = 0.631 \times 10^{-4}$ M.

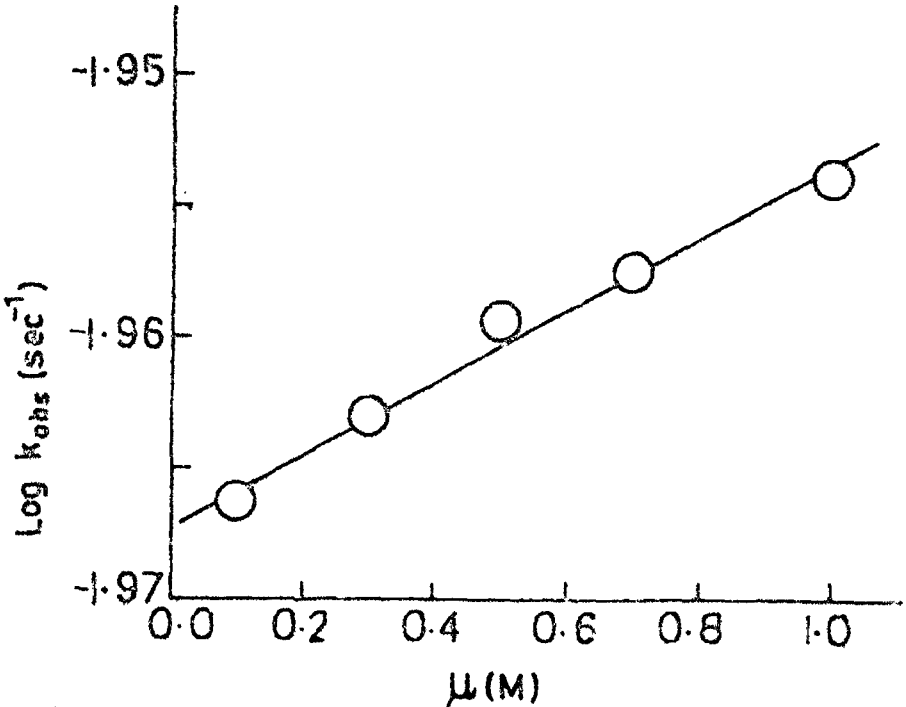


Fig.14: Dependence of rate constant (k_{obs}) on ionic strength (μ) at 45 °C; $[Cr^{3+}] = 3 \times 10^{-3}$ M; [Aspartic acid]$_T$ = 0.06 M, $[H^+] = 1.0 \times 10^{-4}$ M.

Discussions

It is now well established that substitution reactions of octahedral complexes of divalent metal ions follow a mechanism which is largely dissociative in nature. Consequently, the substitution rates of complex formation reactions of a divalent metal-aquo ion with simple ligands do not show an appreciable ligand dependence.[2]

For Cu^{2+} which does not form complexes of regular octahedral configuration, associative substitution may appear not unlikely. However, studies of the complex formation kinetics of Cu^{2+} with several uncharged N-donating ligands of different basicities yielded second-order rate constants around 5×10^{8} M^{-1} $sec.^{-1}$ and did not give evidence for a associative contribution to the substitution process. Moderate deviations from this value which have been observed in some cases of bidentate ligands are attributed to other factors.

Trivalent transition metal ions do not follow this simple pattern. It is well known that the substitution rates for complex formation reactions of Cr^{3+} vary by several orders of magnitude.[3,4] Differences in rate up-to a factor $\sim$100 have also been reported for the reactions of Fe^{3+} with monovalent anions.[5,6] Studying the complex formation reactions of Ti^{3+} and V^{3+} with a variety of ligands it has been found that also for these metal ions variations in substitution rate upto a factor

of 10^3 do occur. The ligand dependence of the substitution rate which is observed for trivalent transition metal ions indicates a transition state in which bond formation between the metal centre and the incoming ligand has already reached an appreciable extent; i.e. the substitution mechanism is partly associative in character.

Kinetics of substitution reactions of chromium(III) have got a special place from mechanistic point of view. Two different pathways are assigned-dissociative interchange (Id) type[7-12] or associative interchange (Ia) type[13,14]. Swaddle and his collaborators[15-17] have studied the substitution reactions of Cr(III) complexes with varying ligands and always found an associative interchange (Ia) process. Substitution reactions (excluding base hydrolysis and trans-activated reactions) of cationic octahedral trivalent transition metals are fully consistent with the operation of an Ia mechanism for all cases examined in detail to date, except for Co(III) complexes(Id). Data on vanadium(III)[18], molybdenum (III)[19] and ruthenium(III)[20] support this generalisation, in addition to the chromium(III), rhodium(III) and iridium(III). For iron (III) too, the anation rate constant of hexaaquo complex in water is dependant upon the nature of incoming ligand[21], as expected for an Ia process. The simple hypothesis that a change in the general mechanism of simple substitution of octahedral cations from Id to Ia occurs on going from divalent to trivalent transition metals (other than cobalt),

is actually entirely reasonable in terms of simple concepts of mechanistic preference based on the charge density at the metal centre.[22] The charge density may be gauged by the charge/radius ratio, and is therefore much greater on M(III) centres relative to M(II) by virtue of their markedly smaller ionic radii,[23,24] as well as their higher oxidation state. Thus, even though Id processes may be universal for M(II) substitutions, Ia mechanisms can be anticipated for M(III) and M(IV), etc.

The anamolous behavior of the cobalt(III) is probably due to the fact that the spin-paired Co^{3+} ion has the smallest crystal ionic radius of all the trivalent transition metals,[25] and it is known[26] that severe steric strain exists even in the ground state of such a simple complex as $Co(NH_2CH_3)_5Cl^{2+}$. Accordingly, steric compression will favour dissociative and supress associative processes in Co(III) complexes.

Later Swaddle[27] has reviewed the activation parameters and mechanism of octahedral substitution reactions and has concluded that an Ia mechanism is operative for octahedral cationic complexes of all trivalent metal ions (except Co(III)) having ionic radii greater than ca.60 pm (but Id for very largest tripositive ions where charge-to-radius ratio is again small as for divalent cations in which Id mechanism operates). The "field-free" radius of Cr^{3+} is 68-69 pm.[24]

It is well known that complex formation of metal ions with ligands in solution proceeds in successive steps.[28,29] In the reaction of chromium(III) with amino acids (monoamino, monocarboxylic acids) formation of more than one complex has been obtained (excepting glycine). Successive steps of complex formation could be represented by the reactions:

$$Cr^{3+} + L^- \rightleftharpoons CrL^{2+} \qquad (1)$$

$$CrL^{2+} + L^- \rightleftharpoons CrL_2^+ \qquad (2)$$

$$CrL_2^+ + L^- \rightleftharpoons CrL_3 \qquad (3)$$

These reactions are written with the anionic form of amino acid (L^-) because it is generally believed that only the anion is reactive for the metal complex formation although other forms do exist in high concentrations.[30] On the other hand, some experimental evidence of complex formation with zwitterion has been given[31-35] but the kinetic studies are very limited.[35-37]

It is well known that depending on the pH of the solution amino acids take the form of cation, zwitterion or anion:[38]

$$H_2L^+ \xleftarrow[K_1]{H^+} HL \xleftarrow[K_2]{H^+} L^-$$

Under our experimental conditions, which ranges between pH 2.9 and 4.5, the major species are the cation, H_2L^+, and zwitterion,

HL. That this is indeed the case and that the concentration of anionic form is very low, has been clearly shown by Harada et al.[35] for the simplest amino acid-glycine. They have plotted the actual distribution curves of different species against pH using Kings' data[39] of acid and base dissociation constants of glycine.

As discussed in Chapter-III that the zwitterion ligand exists in a relatively high concentration in monoamino, monocarboxylic acids under our experimental conditions, the complex formation between Cr^{3+} and these amino acids (through the carboxyl group) can be expressed as:

$$Cr^{3+} + n\,LH \rightleftharpoons Cr(LH)_n^{3+} \quad (n = 1, 2 \text{ or } 3)$$

which is coupled with the acid dissociation equilibrium of the acid:

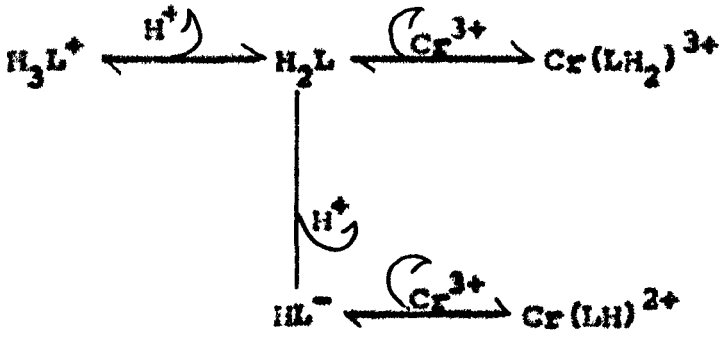
$$n\,H_2L^+ \xleftarrow{nH^+} n\,HL \xleftarrow{Cr^{3+}} Cr(LH)_n^{3+}$$

With aspartic acid (which is a monoamino, di-carboxylic acid) the complex formation can be shown as:

$$Cr^{3+} + LH_2 \rightleftharpoons Cr(LH_2)^{3+}$$

$$Cr^{3+} + LH \rightleftharpoons Cr(LH)^{2+}$$

which is coupled with the acid dissociation equilibria:



(which of the two complexes , namely $Cr(H_2L)^{3+}$ or $Cr(HL)^{2+}$, predominates will depend upon pH which is the deciding factor of the relative abundance of species H_2L or HL^-).

Mechanism of anation of $Cr(H_2O)_6^{3+}$ by monoamino, monocarboxylic acids.

The dependence of pseudo-first-order rate constants (k_{obs}) on[ligand] and $[H^+]$ is consistent with an ion-pair mechanism (the so-called 'Eigen Mechanism')[40] which could be envisaged as follows:

$$H_2L^+ \rightleftharpoons HL + H^+ \qquad (1)$$

$$(H_2O)_6Cr^{3+} + LH \overset{K_{IP}}{\rightleftharpoons} (H_2O)_6Cr^{3+},LH \qquad (2)$$

$$(H_2O)_6Cr^{3+},LH \xrightarrow{k_{an}} (H_2O)_5CrLH^{3+} + H_2O \qquad (3)$$

$$Cr(H_2O)_5LH^{3+} \xrightarrow[fast]{ligand} \text{Higher complexes} \qquad (4)$$

The rate equation derived on the basis of above mechanism is:

$$k_{obs} = \frac{d\ln[complex]}{dt} = \frac{k_{an} K_{IP} K_a [Amino\ acid]_T}{[H^+] + K_a + K_{IP} K_a [Amino\ acid]_T} \qquad (5)$$

where $[Amino\ acid]_T$ is the total concentration of the added monoamino, monocarboxylic acid. By rearranging equation (5) we get equation (6) :

$$\frac{1}{k_{obs}} = \frac{1}{k_{an}} + \frac{[H^+] + K_a}{k_{an} K_{IP} K_a [Amino\ acid]_T} \qquad (6)$$

Accordingly, a plot of k_{obs}^{-1} against $[Amino\ acid]_T^{-1}$ would result in a straight line. Also, such a plot would have a constant intercept for different values of pH. This is indeed the case as is clear from Figs. 15-27.

The values of k_{an} and K_{IP} could be evaluated from the intercepts and slopes of the plots in Figs.15-27. These rate parameters were calculated by linear least-square regression analysis of the data, using IBM 1130 computer (Programme No.2, Appendix). The results are summarised in Tables 14-18.

For the anation rate constants (k_{an}) the activation parameters were obtained from plots of log ($k_{an}Nh/RT$) against 1/T (Figs.28-32). Thermodynamic parameters for K_{IP} were evaluated from the plots of log K_{IP} against 1/T. In the present work the values of k_{an} (with all the amino acids) are found

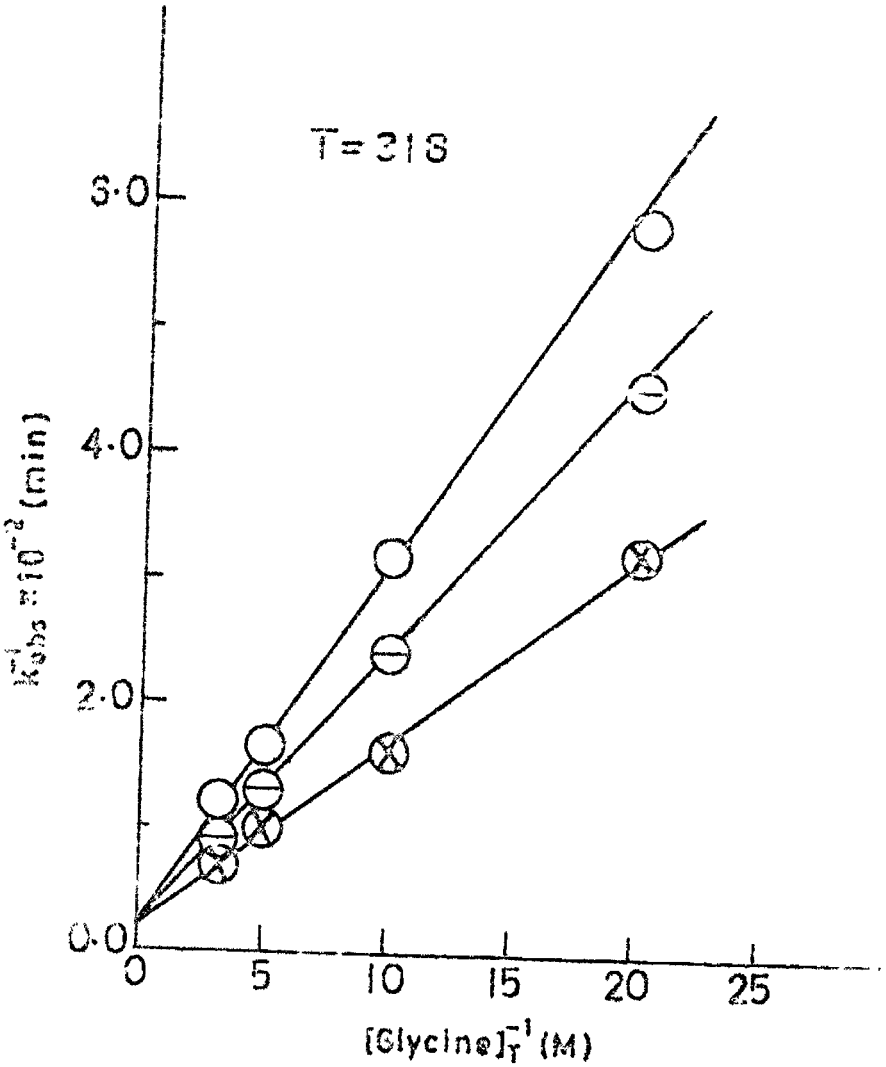


Fig.15: Dependence k^{-1}_{obs} on $[Glycine]^{-1}_T$; $[Cr^{3+}] = 5.00 \times 10^{-3}$M, $\mu = 1.0$M and $[H^+] = 7.782 \times 10^{-4}$M—◯ : 2.59×10^{-4}M—⊖, 0.100×10^{-4}M—⊗.

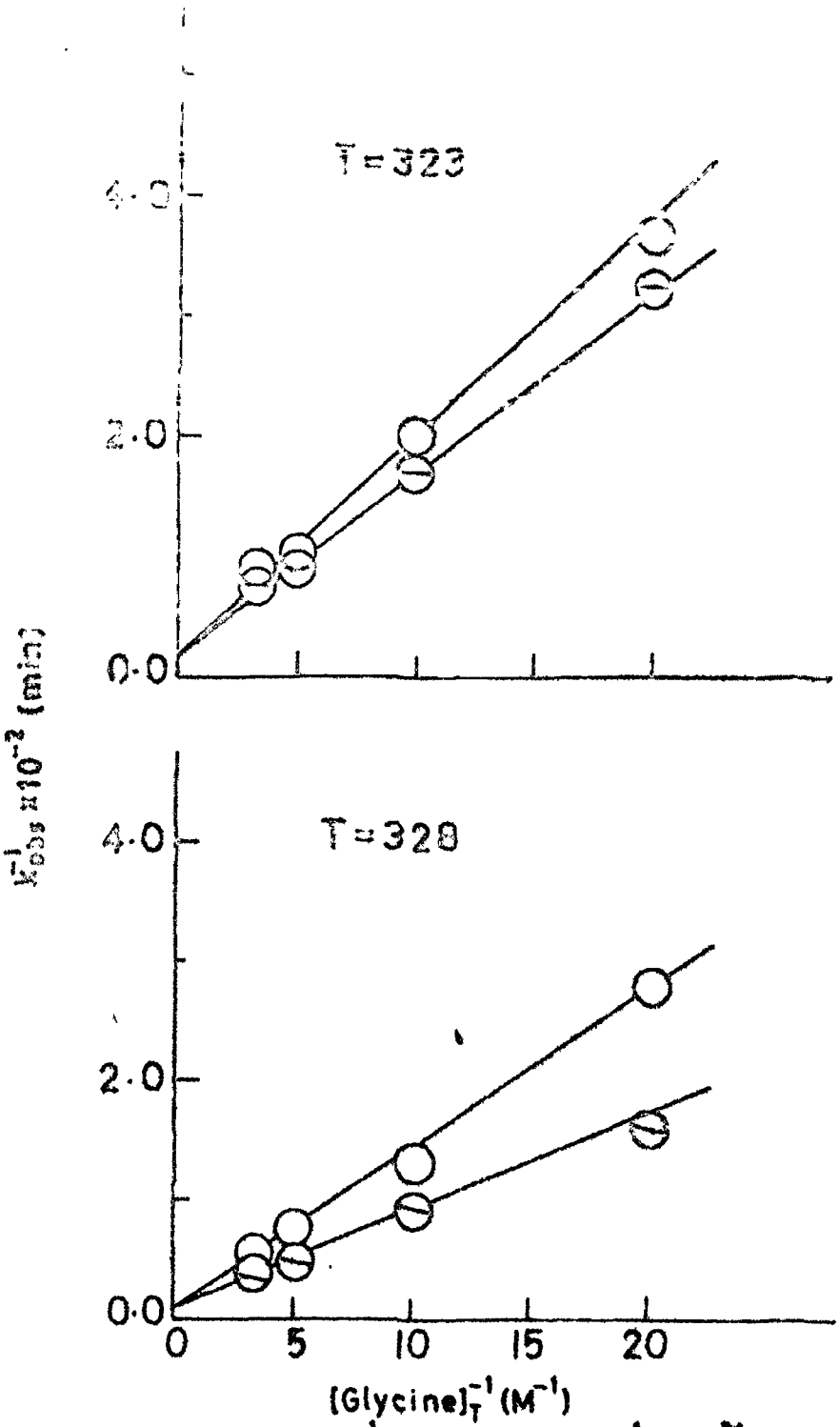


Fig.16: Dependence of k_{obs}^{-1} on $[Glycine]_T^{-1}$; $[Cr^{3+}] = 5.00 \times 10^{-3}$ M, $\mu = 1.0$ M and $[H^+] = 7.782 \times 10^{-4}$ M — ◯, 1.259×10^{-4} M — ⊖.

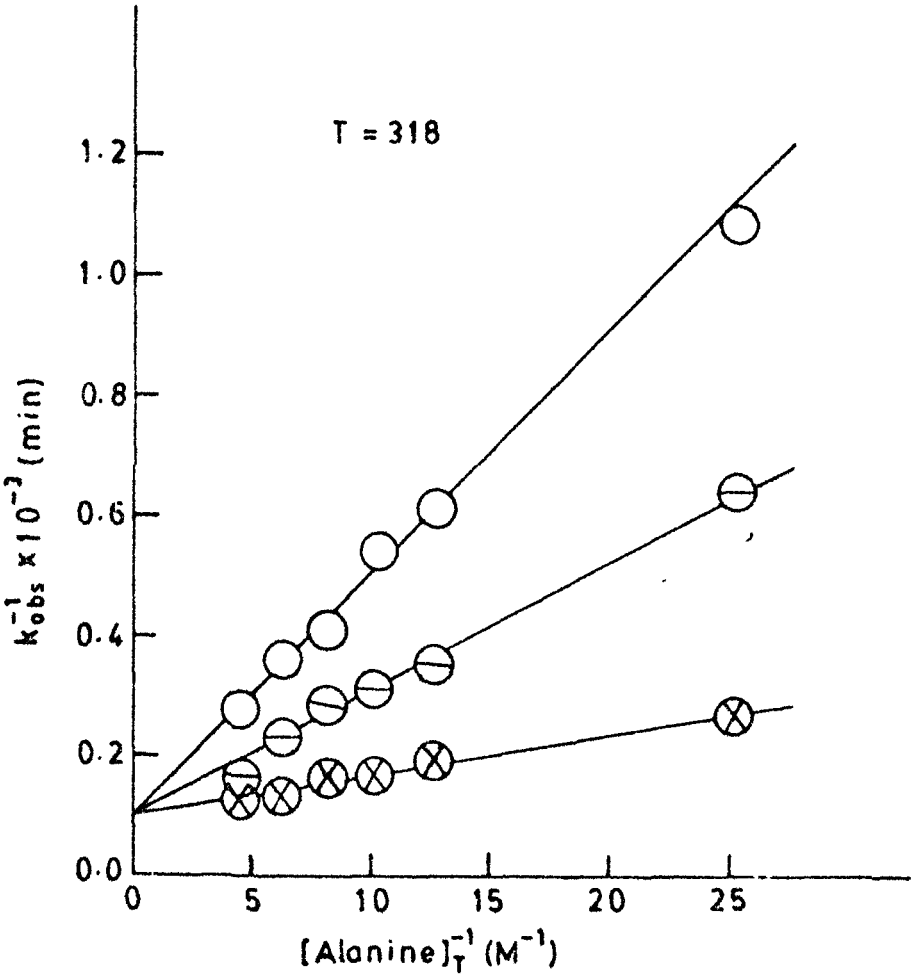


Fig.17: Dependence of k_{obs}^{-1} on $[Alanine]^{-1}$; $[Cr^{3+}] = 4.0 \times 10^{-3}$ M, $\mu = 1.0$ M and $[H^+] = 5.012 \times 10^{-4}$ M-◯, 1.581×10^{-4} M-⊖, 0.398×10^{-4} M-⊗.

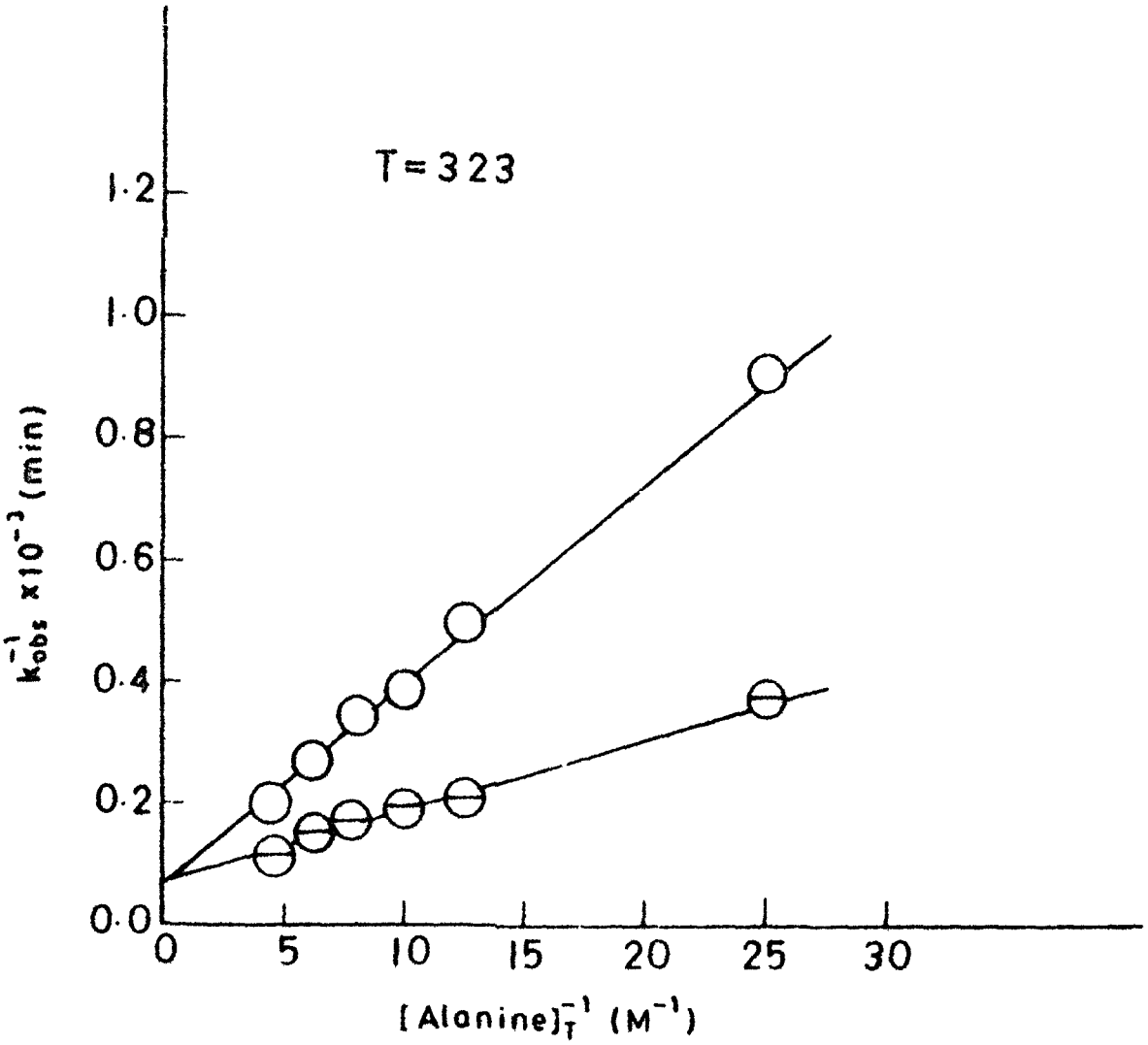


Fig.18: Dependence of k_{obs}^{-1} on $[Alanine]_T^{-1}$; $[Cr^{3+}] = 4.0 \times 10^{-3}$ M, $\mu = 1.0$ M and $[H^+] = 5.012 \times 10^{-4}$ M–○, 1.581×10^{-4} M–⊖.

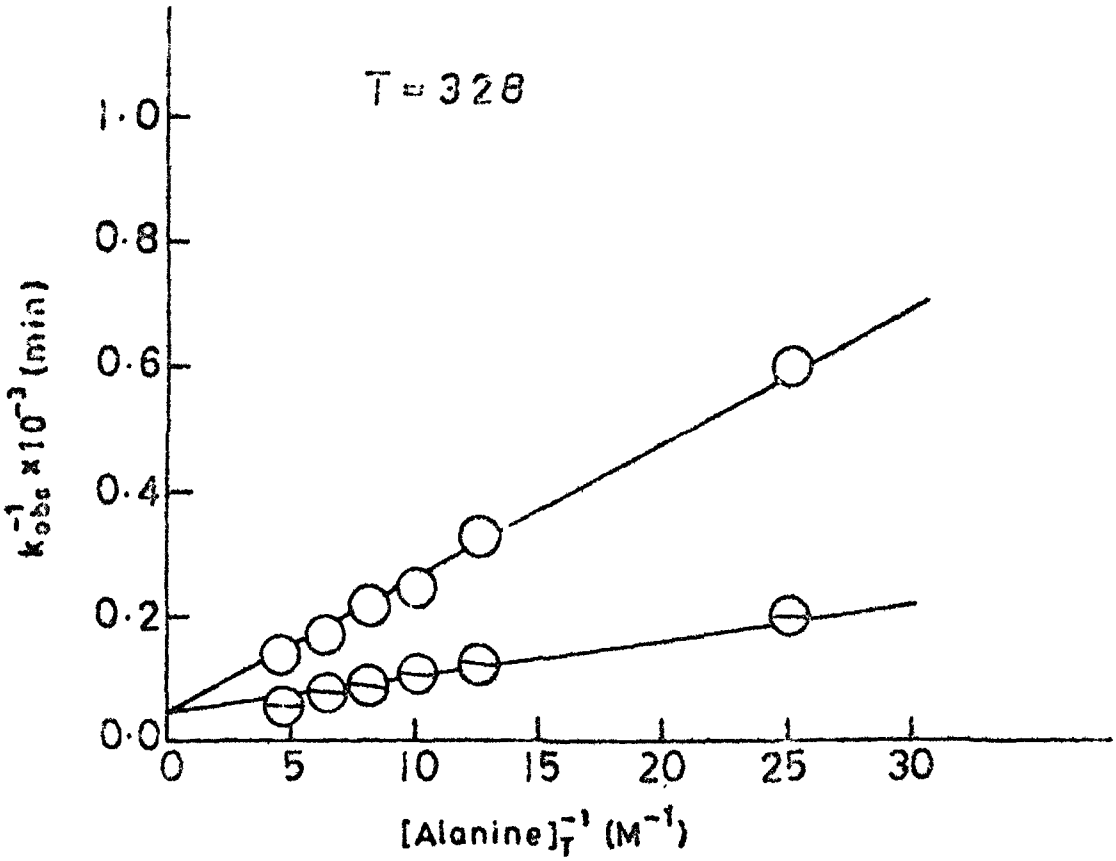


Fig.19 : Dependence of k_{obs}^{-1} on [Alanine]$^{-1}$; $[Cr^{3+}] = 4.0 \times 10^{-3}$ M, $\mu = 1.0$ M and $[H^+] = 5.012 \times 10^{-4}$ M–○, 1.585×10^{-4} M–⊖.

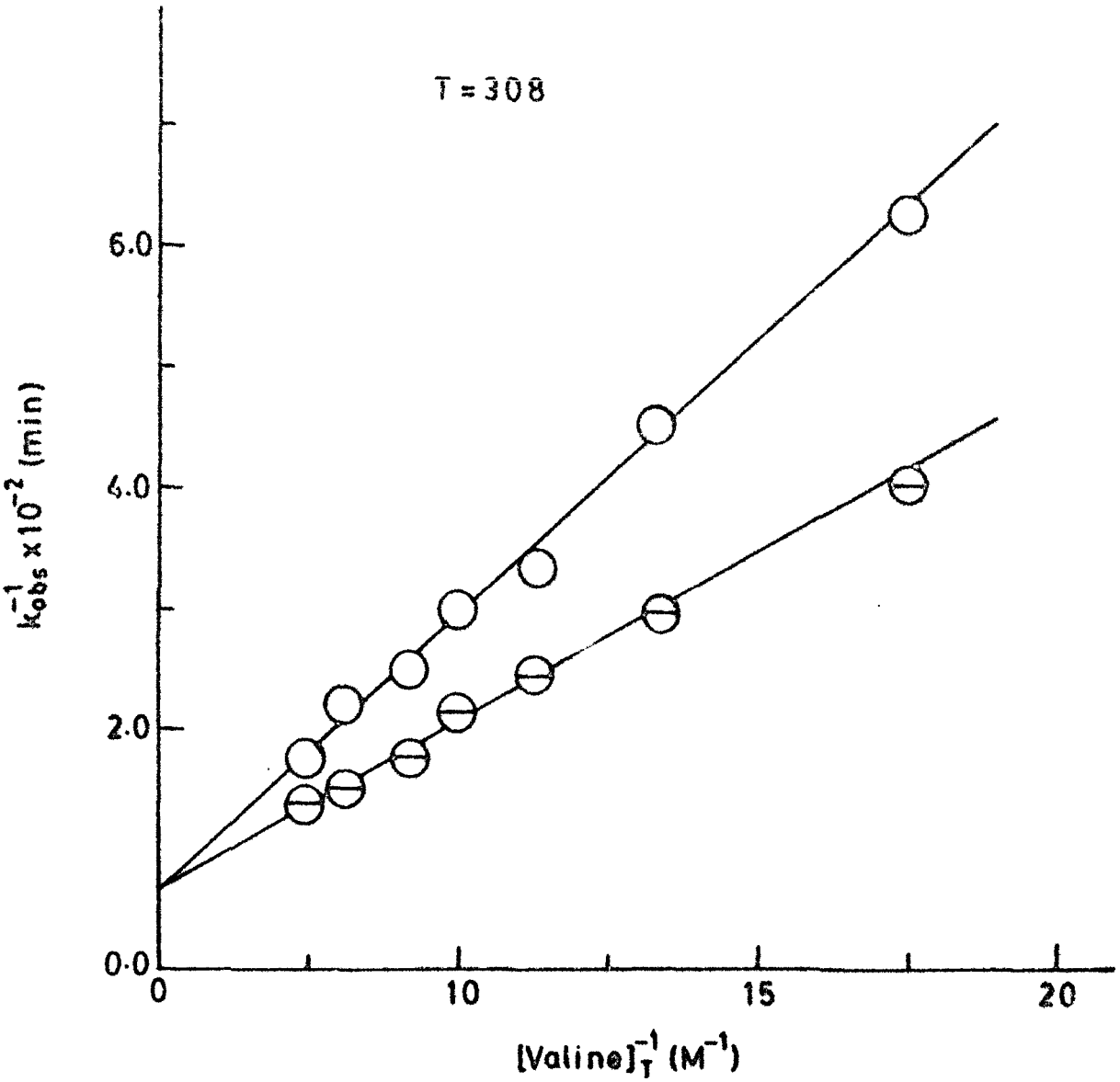


Fig.20: Dependence of k_{obs}^{-1} on $[Valine]_T^{-1}$; $[Cr^{3+}] = 4.0 \times 10^{-3}$ M, $\mu = 1.0$ M and $[H^+] = 2.512 \times 10^{-4}$ M– ◯, 1.585×10^{-4} M–⊖.

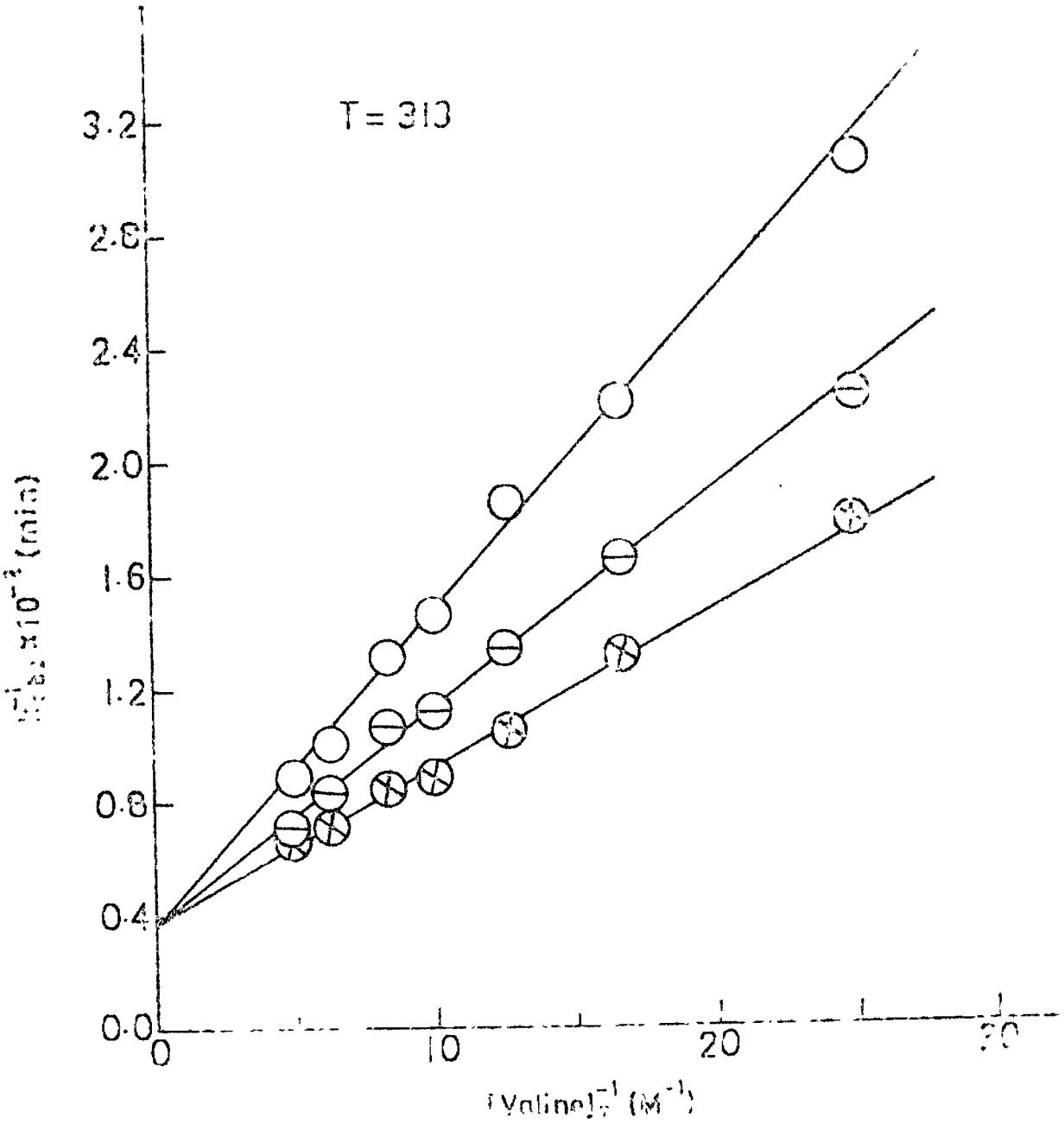


Fig.21: Dependance of k_{ob}^{-1} on [Valine]$_T^{-1}$; [Cr^{3+}] = 4·0×10^{-2} M, μ = 1·0 M and [H^+] = 2·931×10^{-4} M — ○ 2·512 M — ⊖ 1·585 M — ⊗

Fig.22: Dependence of k_{obs}^{-1} on $[Valine]_T^{-1}$; $[Cr^{3+}] = 4.0 \times 10^{-3}$ M, $\mu = 1.0$ M and $[H^+] = 3.981 \times 10^{-4}$ M – ◯, 2.512 M – ⊖, 1.585 M – ⊗.

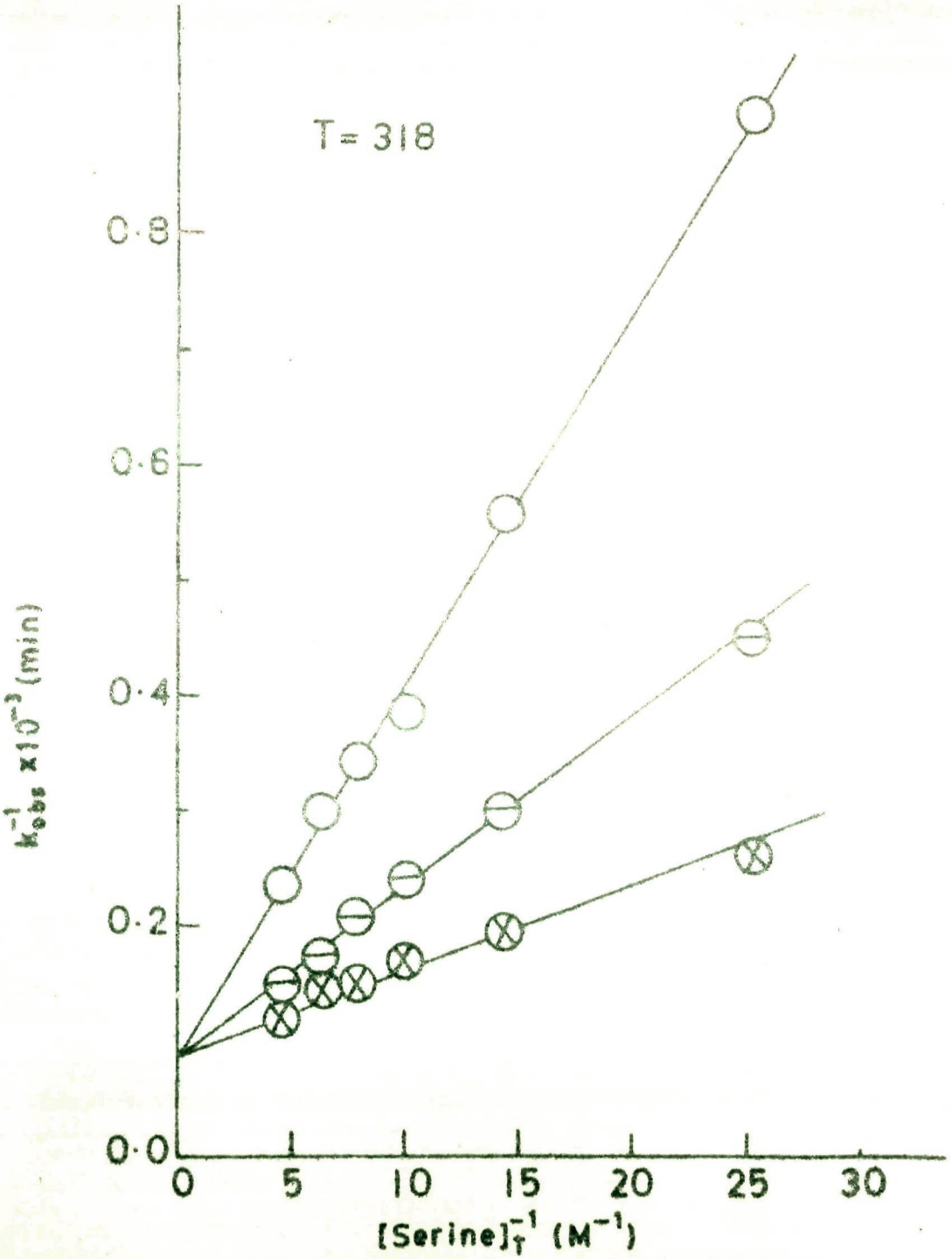


Fig.23: Dependence of k_{obs}^{-1} on $[Serine]_T^{-1}$; $[Cr^{3+}] = 4.00 \times 10^{-3}$M, $\mu = 1.0$M and $[H^+] = 12.59 \times 10^{-3}$M—○ 4.467×10^{-4}M— ⊖ 1.413×10^{-4} M—⊗.

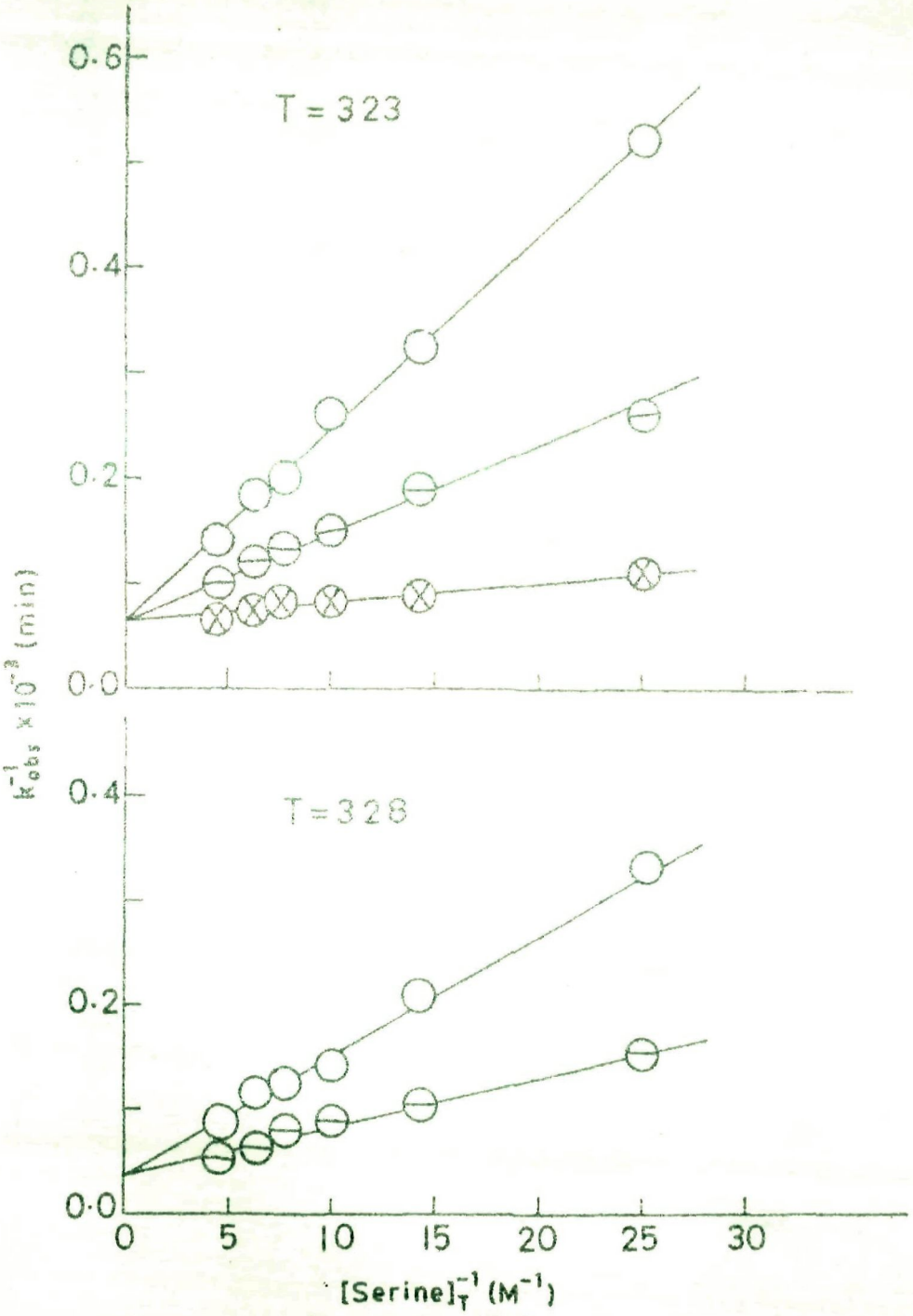


Fig.24: Dependence of k^{-1}_{obs} on $[Serine]^{-1}_T$ at indicated temperatures; $[Cr^{3+}] = 4{\cdot}0 \times 10^{-3}$ M, $\mu = 1{\cdot}0$ M and $[H^+] = 12{\cdot}59 \times 10^{-3}$ M — ◯ $4{\cdot}467 \times 10^{-4}$ M — ⊖ $1{\cdot}413 \times 10^{-4}$ M — ⊗.

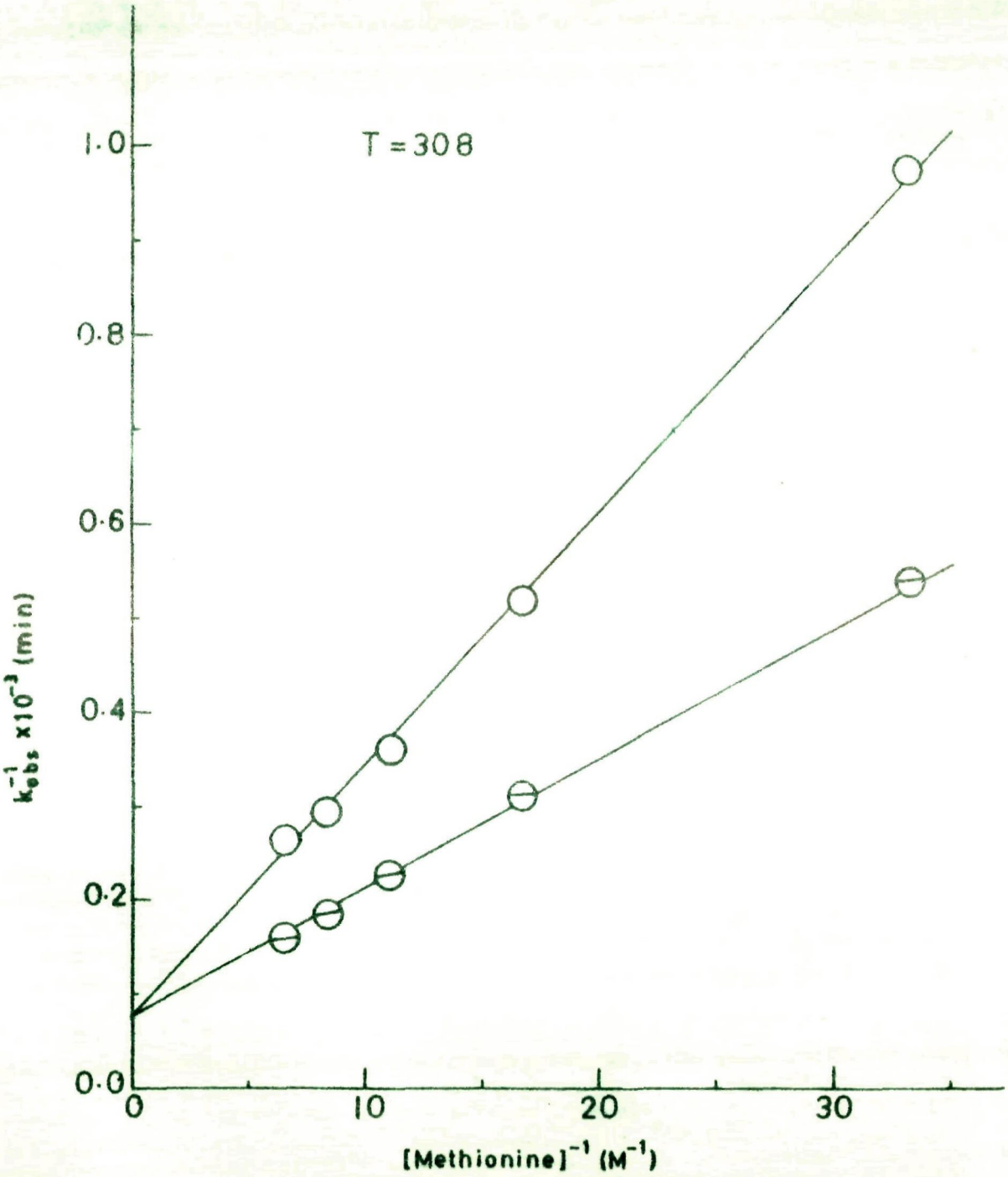


Fig.25: Dependence of k_{obs}^{-1} on [Methionine]$^{-1}$; $[Cr^{3+}] = 3{\cdot}0 \times 10^{-3}$ M, $\mu = 1{\cdot}0$ M and $[H^+] = 1{\cdot}585 \times 10^{-4}$ M—○ $0{\cdot}631 \times 10^{-4}$ M—⊖.

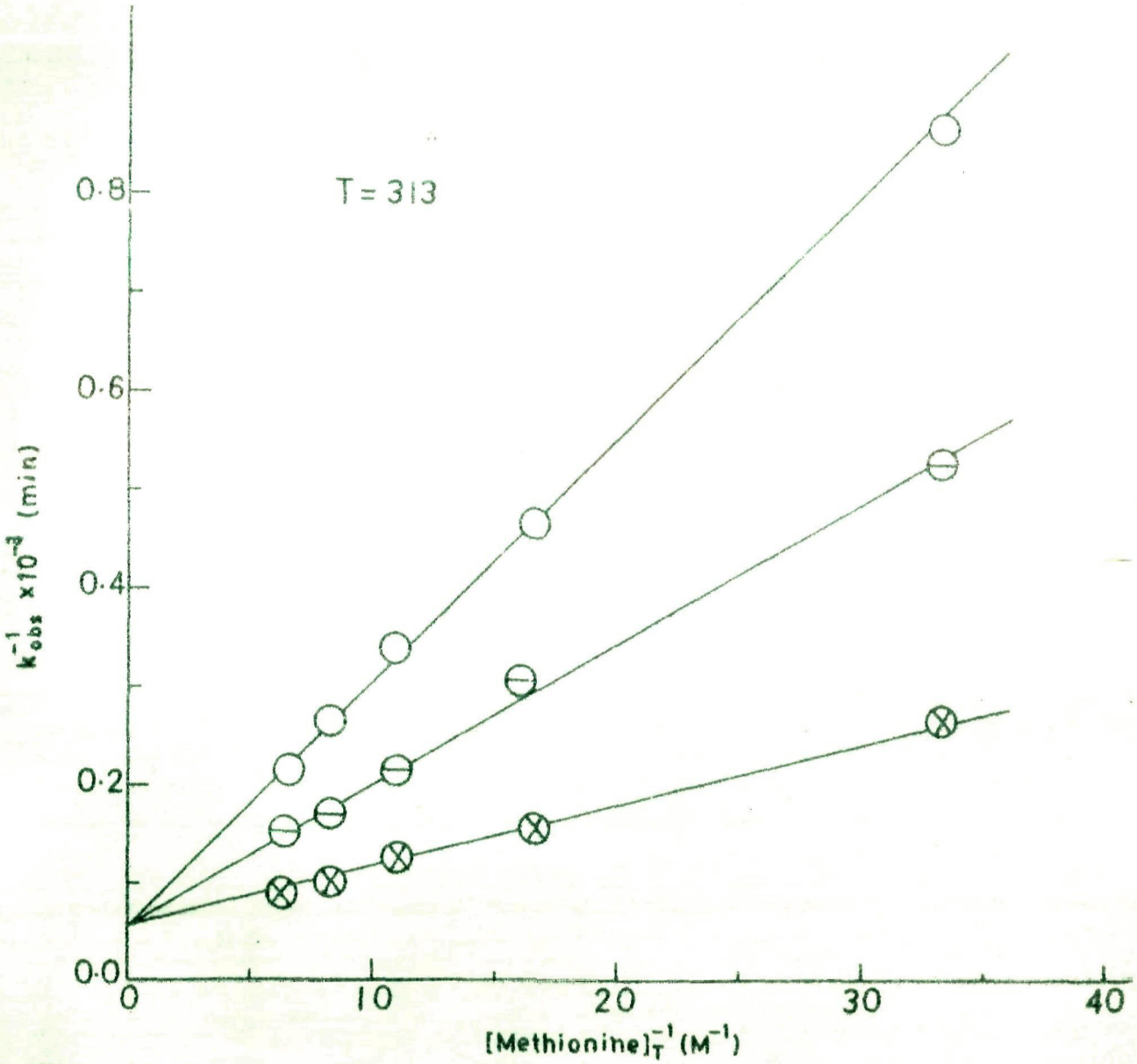


Fig.26: Dependence of k^{-1}_{obs} on $[Methionine]^{-1}_T$; $[Cr^{3+}] = 3{\cdot}0 \times 10^{-3}$ M, $\mu = 1{\cdot}0$ M and $[H^+] = 3{\cdot}981 \times 10^{-4}$ M—◯, $1{\cdot}585 \times 10^{-4}$ M—⊖, 0·631 M—⊗.

Fig.27: Dependence of k^{-1}_{obs} on [Methionine]$_T^{-1}$; $[Cr^{3+}] = 3{\cdot}0 \times 10^{-3}$ M, $\mu = 1{\cdot}0$ M, and $[H^+] = 3{\cdot}981 \times 10^{-4}$ M—◯, $1{\cdot}585 \times 10^{-4}$ M—⊖, 0·631 M—⊗.

TABLE-14. Rate parameters calculated from the data given in Table 8 for the reaction of chromium(III) with glycine.

Temp. (°C)	10^4. k_{an} (sec^{-1})	K_{IP} (M^{-1})	10^3. K_a † (M)	10^6. k_{ex} †† (sec^{-1})
35	-	-	-	4.17
45	8.33	0.91	4.87	
50	11.12	1.01	4.91	
55	16.66	1.26	4.92	

† B.B. Owen J.Am. Chem. Soc., 56 (1934) 24.

†† R.A. Plane and H. Taube, J. Phys. Chem., 56 (1952) 33.

TABLE-15. Rate parameters calculated from the data given in Table 9 for the reaction of chromium(III) with DL-∝-alanine.

Temp. (°C)	$10^4 \cdot k_{an}$ (sec^{-1})	K_{IP} (M^{-1})	$10 \cdot K_a$ † (M)	$10^6 \cdot k_{ex}$ †† (sec^{-1})
35	-	-	-	4.17
45	1.81	3.64	4.76	-
50	3.33	1.62	4.78	-
55	6.01	1.28	4.83	-

† Extrapolated values from the date of L.F. Nims and P.K. Smith, J.Biol. Chem., 101 (1933) 401.

†† R.A. Plane and H. Taube, J. Phys. Chem., 56 (1952) 33.

TABLE-16. Rate parameters calculated from the data given in Table 10 for the reaction of chromium(III) with DL-valine.

Temp. (^{o}C)	10^{4}. k_{an} (sec^{-1})	K_{IP} (M^{-1})	10^{3}. $K_{a}^{\dagger}$ (M)	10. $k_{ex}^{\dagger\dagger}$ (sec^{-1})
35	2.56	4.87	6.72	4.17
40	4.38	7.20	7.08	-
45	7.24	11.64	7.11	-

† Extrapolated values from the data of P.K. Smith, A.C. Taylor and E.R.B. Smith, J. Biol. Chem., 122 (1937) 109.

†† R.A. Plane and H. Taube, J. Phys. Chem., 56 (1952) 33

TABLE-17. Rate parameters calculated from the data given in Table 11 for the reaction of chromium(III) with DL-serine.

Temp. (°C)	10^4. k_{an} (sec^{-1})	K_{IP} (M^{-1})	10^3. K_a† (M)	10^6. k_{ex}†† (sec^{-1})
35	-	-	-	4.17
45	1.96	4.86	7.24	-
50	2.77	6.66	7.28	-
55	4.76	8.04	7.40	-

† Extrapolated values from the date of P.K. Smith, A.T. Gorham and E.R.B. Smith, J. Biol. Chem., 144 (1942) 737.

†† R.A. Plane and H. Taube, J. Phys. Chem., 56 (1952) 33

TABLE-18. Rate parameters calculated from the data given in Table 12 for the reaction of chromium(III) with DL-methionine.

Temp. (^{o}C)	10^{4}. k_{an} (sec^{-1})	K_{IP} (M^{-1})	10^{3}. $K_{a}^{\dagger}$ (M)	10^{6}. $k_{ex}^{\dagger\dagger}$ (sec^{-1})
35	2.22	2.82	5.49	4.17
40	3.01	3.79	5.64	-
45	5.12	4.46	5.75	-

† Values calculated from Harned and Embree equation; J.Am. Chem. Soc., 56 (1934) 1050.

†† R.A. Plane and H. Taube, J. Phys. Chem., 56 (1952) 33.

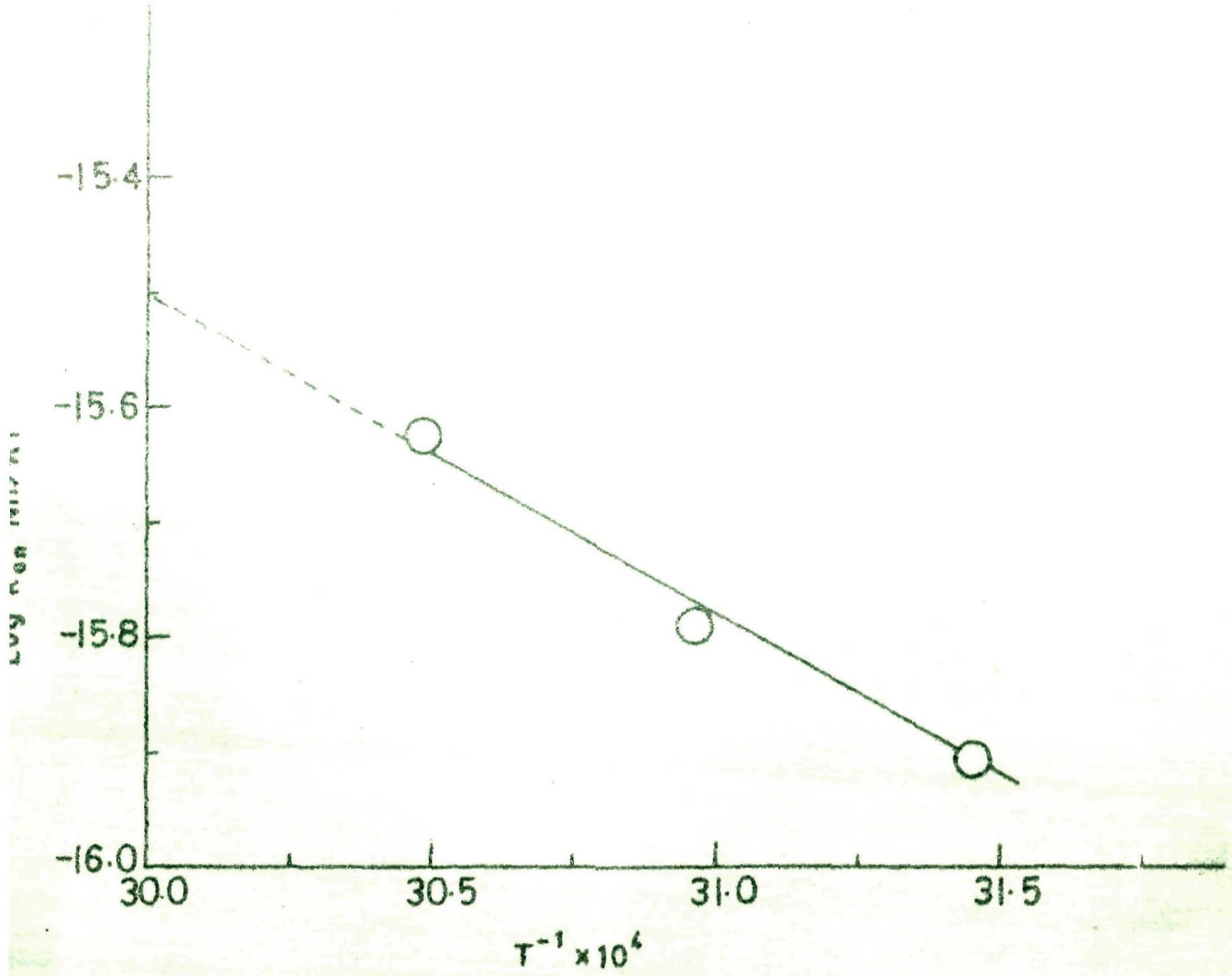


Fig.28: Arrhenius plot for chromium (III) anation with glycine.

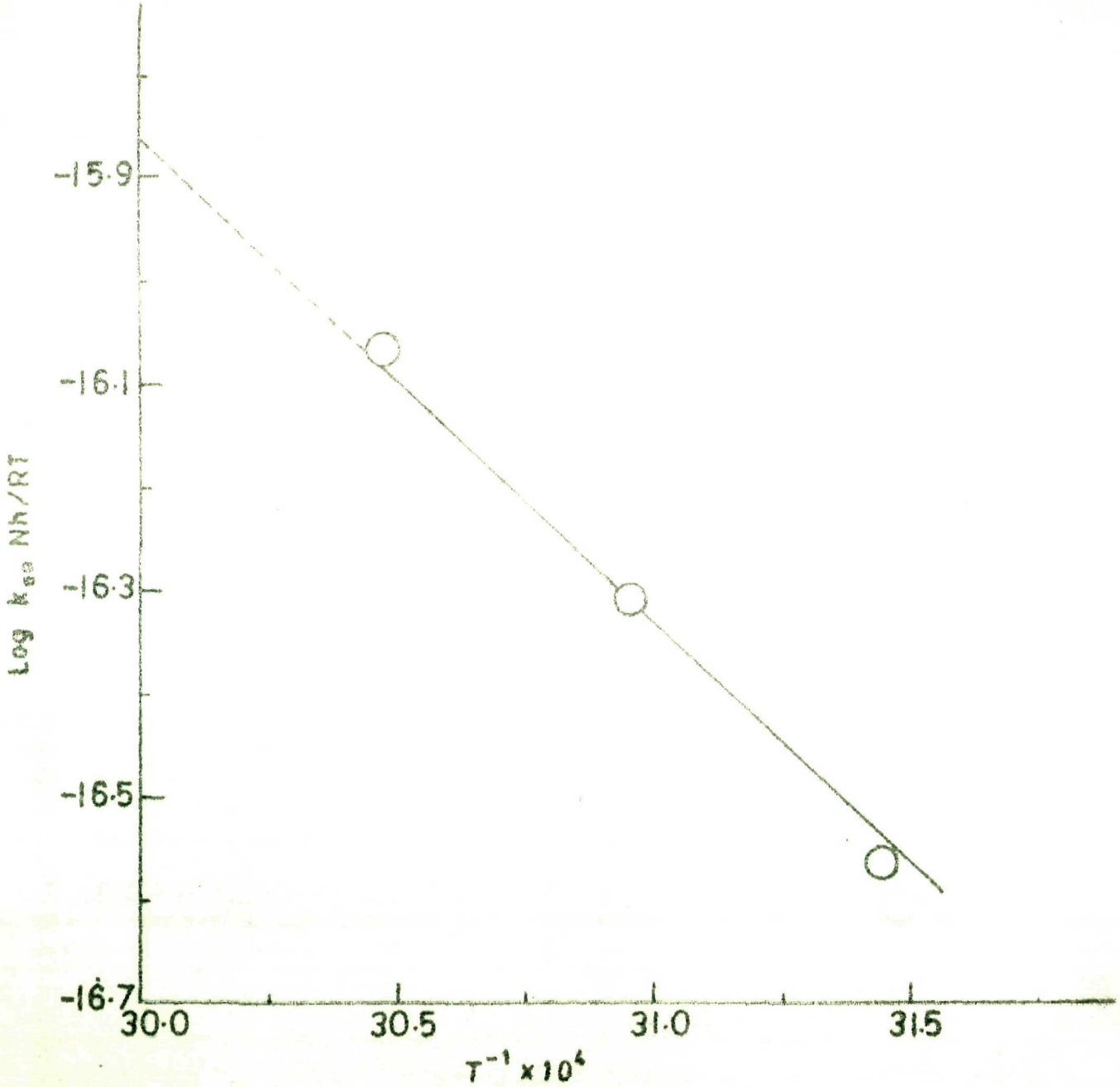


Fig.29: Arrhenius plot for chromium (III) anation with DL-alanine.

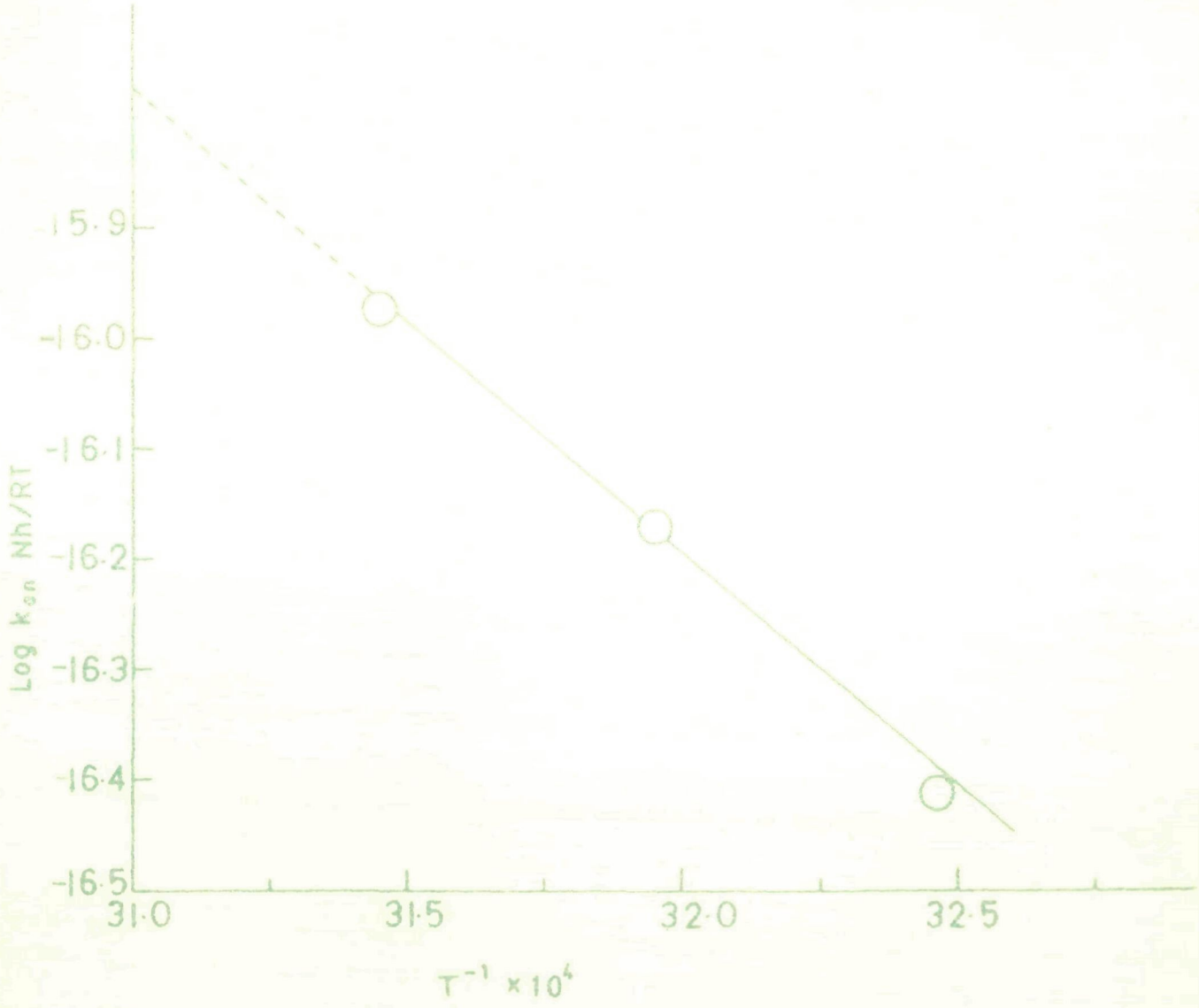


Fig. 30: Arrhenius plot for chromium (III) anation with DL-valine

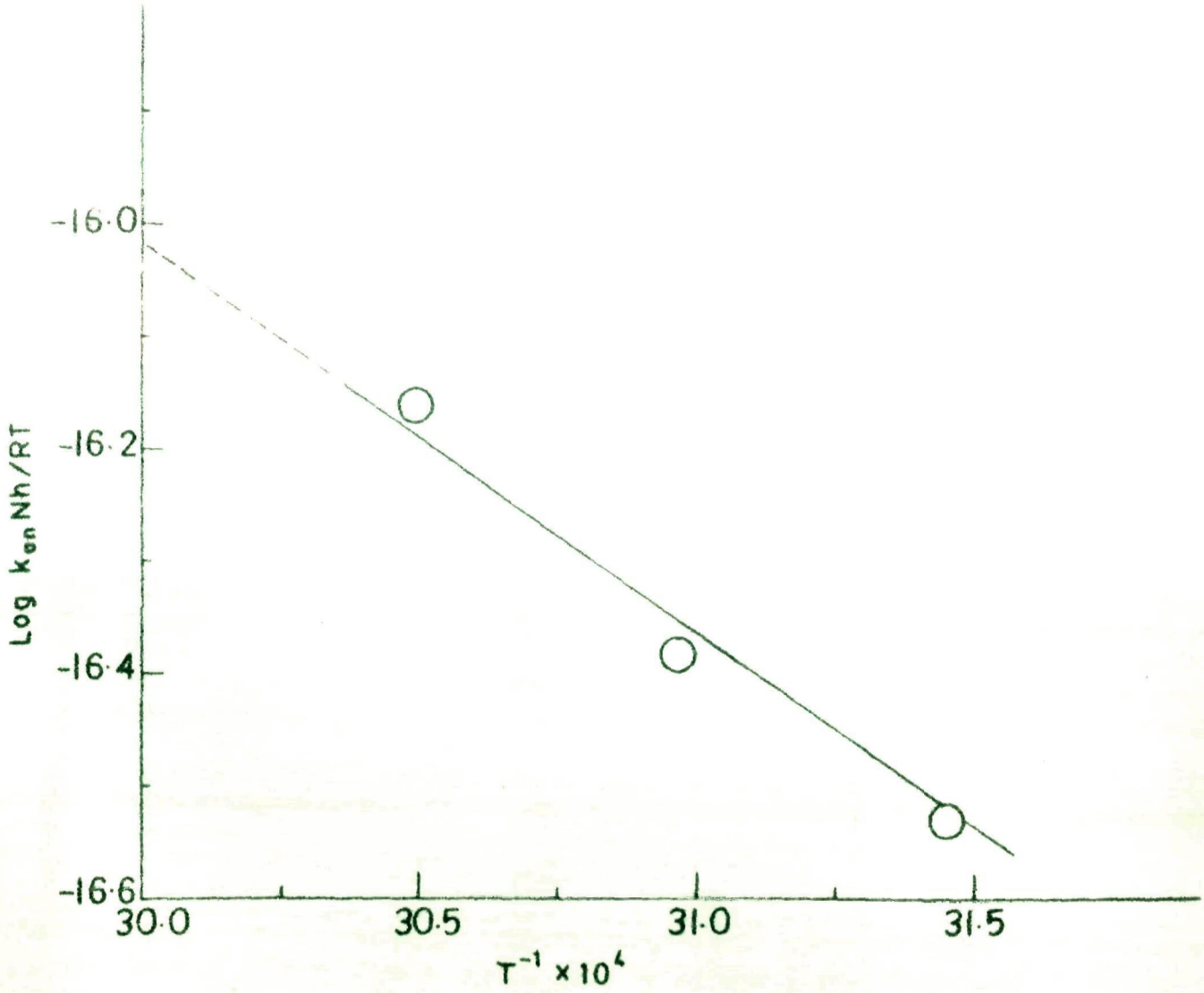


Fig.31: Arrhenius plot for chromium (III) anation with DL-serine.

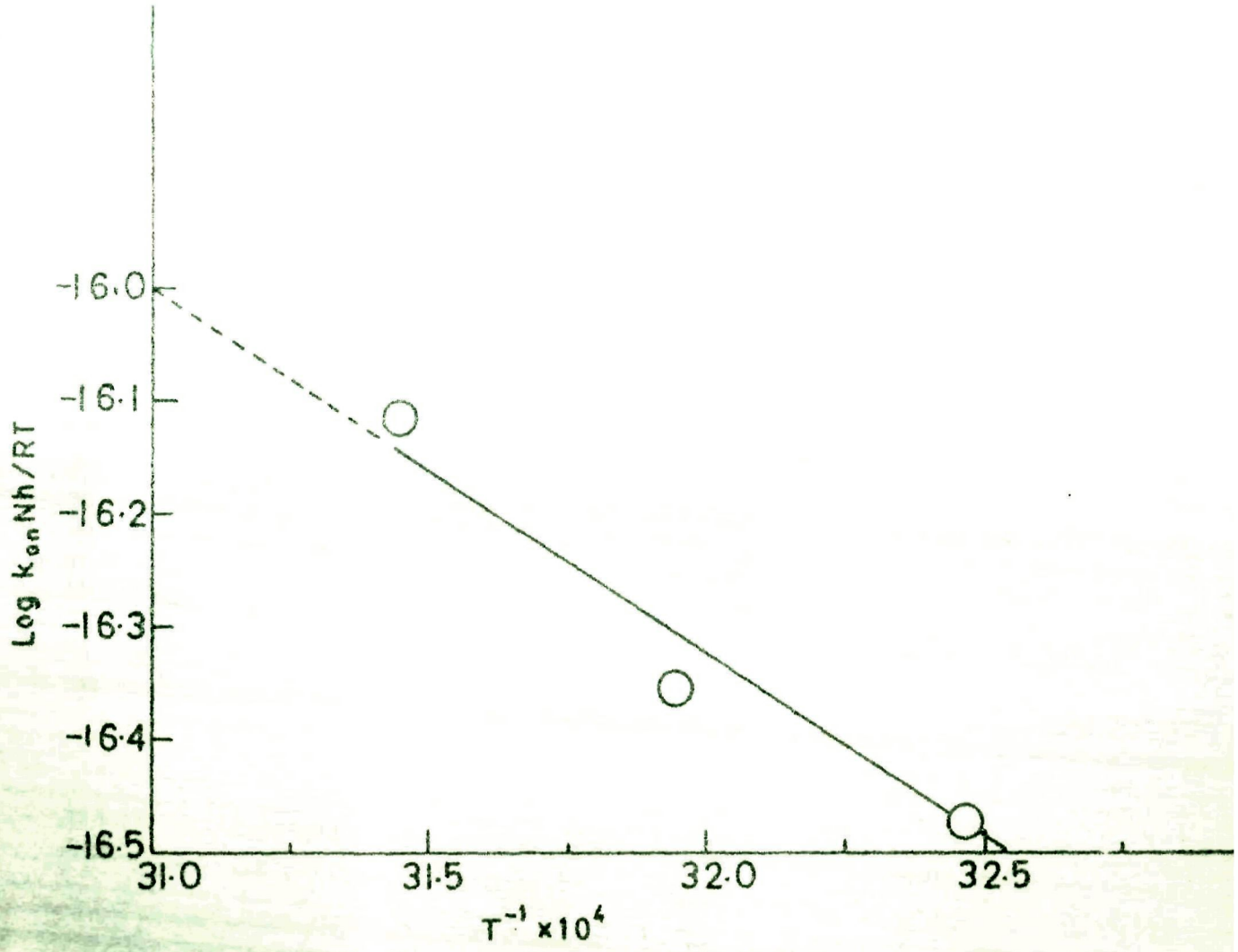


Fig.32: Arrhenius plot for chromium (III) anation with DL-methionine.

to be greater than the value of k_{ex} for water. This suggests a ligand assisted anation and hence associative path of substitution. The rather low enthalpies and large negative entropies (Tables 19-23) further suggest that the reactions are faster than that of water exchange and confirm the Ia mechanism.

The possibility of ion-pairing of the zwitterion with hydroxy species of $Cr(H_2O)_6^{3+}$ has been discarded on the basis of the observed values of K_{IP} which are in a fair agreement with those calculated by Nor and Sykes[41] for a process where part played by hydroxy species is negligible. Also, on the basis of the unfavourable charge factor, ion-pairing of $^{+}H_2L$ with $Cr(H_2O)_6^{3+}$ and the subsequent reactions were assumed to be insignificant.

Mechanism of anation of $Cr(H_2O)_6^{3+}$ by monoamino,dicarboxylic acid.

The mechanism of interaction of hexaaquochromium(III) with aspartic acid (a mono-amino,dicarboxylic acid) is different from that of other amino acids because of the interactions with species H_2L and HL^{-}.

On the basis of variations of the pseudo-first-order rate constants with [Aspartic acid]$_T$ and [H^+] the following mechanism may be proposed:

TABLE-19. Activation parameters for k_{an} and K_{IP} for the reaction of chromium(III) with glycine.

Rate parameters	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.deg.$^{-1}$mole^{-1})	$\Delta G^{\ddagger}$[a] (kcal.mole^{-1})
k_{an} (sec^{-1})	+12.6	-33.2	+23.1
k_{ex}[b] (sec^{-1})	+26.2	+0.3[c]	-
	ΔH^{o} (kcal.mole^{-1})	ΔS^{o} (cal.deg.$^{-1}$mole^{-1})	ΔG^{o} (kcal.mole^{-1})
K_{IP} (M^{-1})	-8.58	-26.6	+0.0

[a] At 45°C

[b] D.R. Stranks and T.W.Swaddle, J.Am.Chem.Soc., 93 (1971) 2783.

[c] Exchange of one ligand only.

TABLE-20. Activation parameters for k_{an} and K_{IP} for the reaction of chromium(III) with DL-α-alanine.

Rate parameters	ΔH^* (kcal.mole^{-1})	ΔS^* (cal.deg.$^{-1}$mole^{-1})	ΔG^{*a} (kcal.mole^{-1})
k_{an}(sec^{-1})	+21.0	-9.3	+24.0
k_{ex}^{b}(sec^{-1})	+26.2	+0.3[c]	-
	ΔH^o (kcal.mole^{-1})	ΔS^o (cal.deg.$^{-1}$mole^{-1})	ΔG^{oa} (kcal.mole^{-1})
K_{IP}(M^{-1})	-18.6	-56.4	-0.7

[a] At 45°C.

[b] D.R.Stranks and T.W.Swaddle, J.Am.Chem.Soc.,93 (1971) 2783.

[c] Exchange of one ligand only.

TABLE-21. Activation parameters for k_{an} and K_{IP} for the reaction of chromium(III) with DL-valine.

Rate parameters	ΔH^{*} (kcal.mole^{-1})	ΔS^{*} (cal.deg.$^{-1}$mole^{-1})	ΔG^{*a} (kcal.mole^{-1})
k_{an}(sec^{-1})	+19.1	-13.1	+23.2
k_{ex}^{b}(sec^{-1})	+26.2	+0.3[c]	-
	ΔH^{o} (kcal.mole^{-1})	ΔS^{o} (cal.deg.$^{-1}$mole^{-1}	ΔG^{oa} (kcal.mole^{-1})
K_{IP}(M^{-1})	-17.6	-49.2	-1.9

[a] At 45 °C

[b] D.R.Stranks and T.W. Swaddle, J.Am.Chem.Soc., 93 (1971) 2783.

[c] Exchange one of ligand only.

TABLE-22. Activation parameters for k_{an} and K_{IP} for the reaction of chromium(III) with DL-serine.

Rate parameters	ΔH^{*} (kcal.mole^{-1})	ΔS^{*} (cal.deg.$^{-1}$mole^{-1}	ΔG^{*a} (kcal.mole^{-1})
k_{an} (sec^{-1})	+15.7	-26.0	+24.0
k_{ex}[b] (sec^{-1})	+26.2	+0.3[c]	-
	ΔH^{o} (kcal.mole^{-1})	ΔS^{o} (cal.deg.$^{-1}$mole^{-1})	ΔG^{oa} (kcal.mole^{-1})
K_{IP} (M^{-1})	-10.7	-30.4	-1.0

[a] At 45°C.

[b] D.R. Stranks and T.W. Swaddle, J.Am.Chem.Soc., 93 (1971) 2783

[c] Exchange of one ligand only.

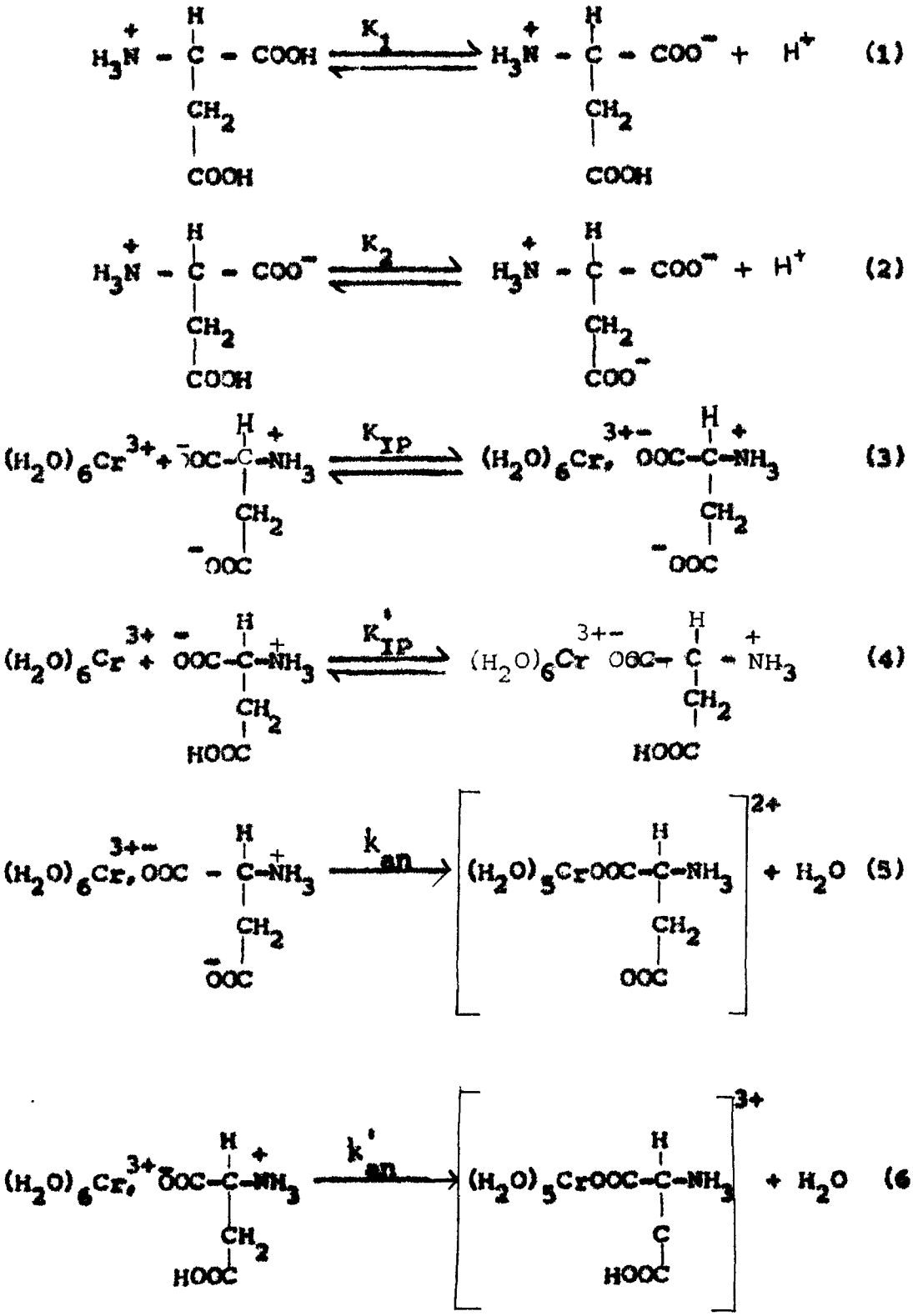
TABLE-23. Activation parameters for k_{an} and K_{ip} for the reaction of chromium(III) with DL-methionine.

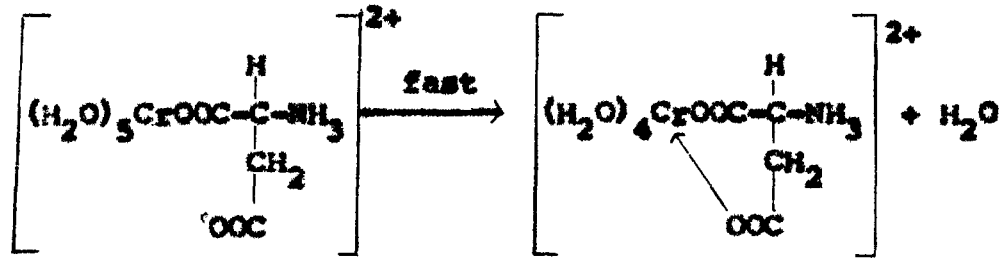
Rate parameters	ΔH^{*} (kcal.Mole^{-1})	ΔS^{*} (cal.deg.$^{-1}$mole^{-1})	ΔG^{*a} (kcal.mole^{-1})
k_{an} (sec^{-1})	+14.6	-27.8	+23.4
k_{ex}^{b} (sec^{-1})	+26.2	+0.3[c]	-
	ΔH^{o} (kcal.mole^{-1})	ΔS^{o} (cal.deg.$^{-1}$mole^{-1})	ΔG^{oa} (kcal.mole^{-1})
K_{ip} (M^{-1})	-15.2	-44.0	-1.2

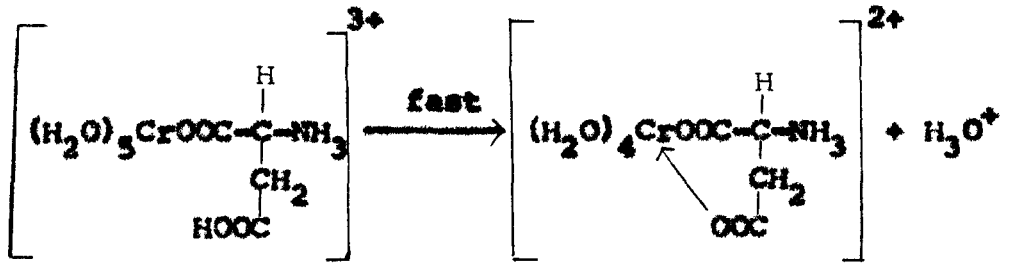
[a] At 45°C

[b] From D.R. Stranks and T.W. Swaddle, J.Am.Chem.Soc., 93(1971) 2783.

[c] Exchange of one ligand only.







The rate equation derived on the basis of above mechanism is:

$$k_{obs} = \frac{d\ln[Complex]}{dt} = \frac{k_{an}K_{IP}K_2 + k'_{an}K'_{IP}[H^+]\ [Aspartic\ acid]_T}{[H^+]^2/K_1 + [H^+] + K_2 + (K_{IP}K_2 + K'_{IP}[H^+])\ [Aspartic\ acid]_T} \qquad (7)$$

where $[Aspartic\ acid]_T$ is the total concentration of aspartic acid added. On rearrangement, equation (7) gives equation (8)

$$\frac{1}{k_{obs}} = \frac{K_{IP}K_2 + K'_{IP}[H^+]}{k_{an}K_{IP}K_2 + k'_{an}K'_{IP}[H^+]} + \frac{[H^+]^2/K_1 + [H^+] + K_2}{k_{an}K_{IP}K_2 + k'_{an}K'_{IP}[H^+]} \cdot \frac{1}{[Aspartic\ acid]_T} \qquad (8)$$

The above mechanism was confirmed by plotting k_{obs}^{-1} vs $[Aspartic\ acid]_T^{-1}$ at different concentrations of hydrogen ion.

The plots (Fig. 33) were found to be linear for a given hydrogen ion concentration. The intercepts of these plots were found to be dependent on $[H^+]$ as is clear from equation(8) (in case of monoamino, monocarboxylic acids a common intercept was obtained at different $[H^+]$).

The values of rate parameters used in equation (7) were calculated and are summarised in Table 24. The values of activation parameters (Fig. 34) calculated for different paths are given in Table 25.

With aspartic acid too, the values of k_{an} and k'_{an} are greater than the value of k_{ex} for water exchange ($4.17 \times 10^{-6} sec^{-1}$) which is indicative that the mechanism is an associative interchange (Ia) type. The values of thermodynamic parameters in Table 25 also support the Ia process as discussed by Swaddle[27] and Sasaki and Sykes[42]. For a series of substitution reactions of related octahedral complexes proceeding via a common Id mechanism, linear correlations of slope $\alpha = 1.0$ should exist between ΔG^* (free energy of the anation rate constant, k_{an}) and ΔG° (free energy for the dissociation constant of the amino acid, K_a). For Ia mechanisms, α should be less than 1.0. A linear free energy relationship was found to be valid for the anation reactions of chromium(III) with all the amino acids (monoamino, monocarboxylic as well as monoamino, dicarboxylic acids). The

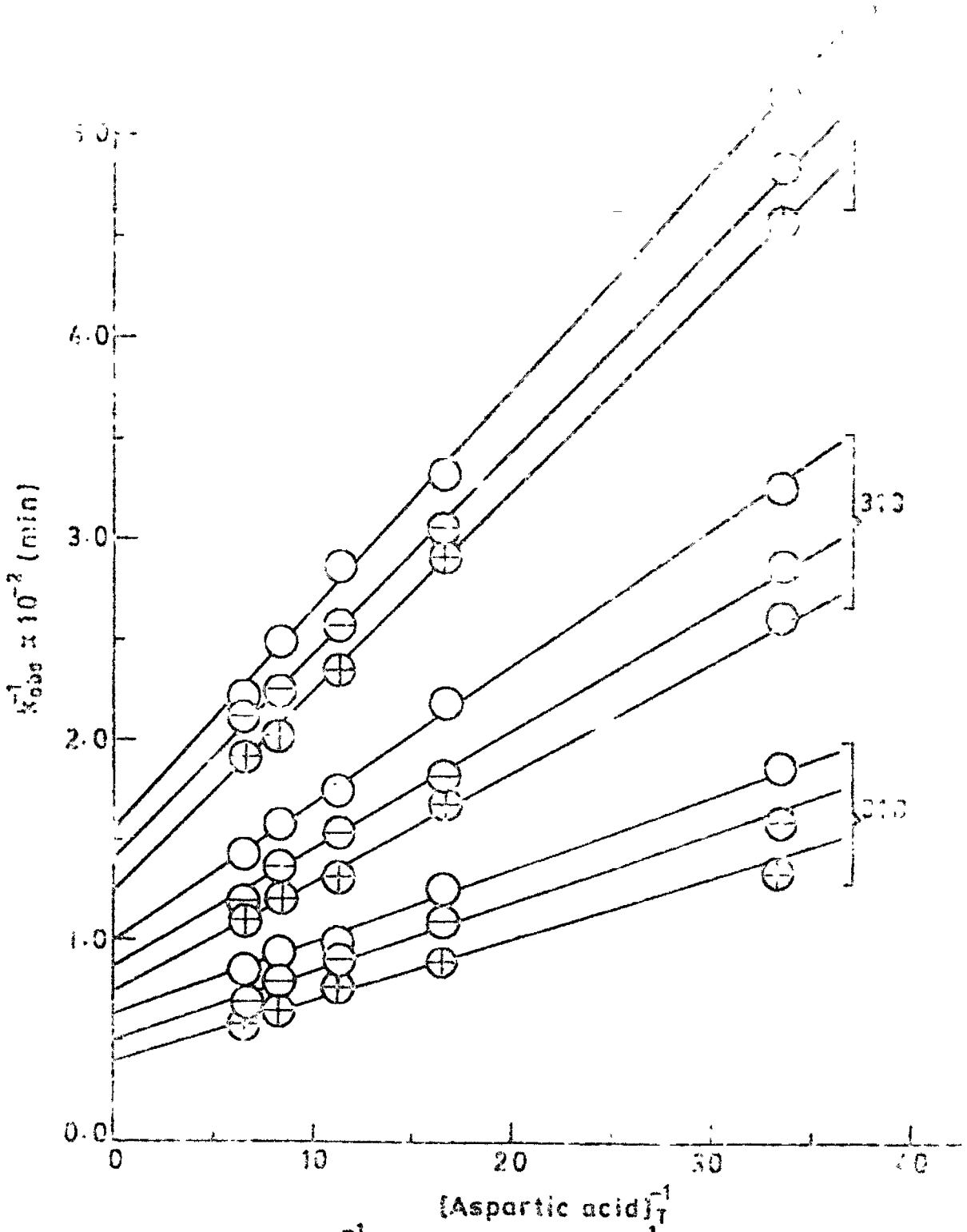


Fig.33: Dependence of k_{obs}^{-1} on [Aspartic acid]$_T^{-1}$ at indicated temperatures; [Cr^{3+}] = 3.0×10^{-3}M, μ = 1.0M and [H^+] = 10.000×10^{-4}M–○, 3.162×10^{-4}M–⊖, 1.000×10^{-4}M–⊕.

TABLE-24. Rate parameters calculated from the data given in Table 13 for the reaction of chromium(III) with DL-aspartic acid.

Temp. (°C)	$10^4.K_{an}$ (sec^{-1})	K_{IP} (M^{-1})	$10^4.K'_{an}$ (sec^{-1})	K'_{IP} (M^{-1})	$10^2.K_1$ † (M)	$10.K_2$ † (M)	$10.k_{ex}$ †† (sec^{-1})
35	2.01	8.51	0.98	6.40	1.12	1.31	4.17
40	3.48	9.78	1.49	7.22	1.15	1.33	-
45	4.76	11.40	2.20	4.67	1.19	1.35	-

† Extrapolated values from the data of P.K. Smith and E.R.B. Smith, J. Biol. Chem., 146 (1942) 187

†† R.A. Plane and H. Taube, J.Phys. Chem., 56 (1952) 33.

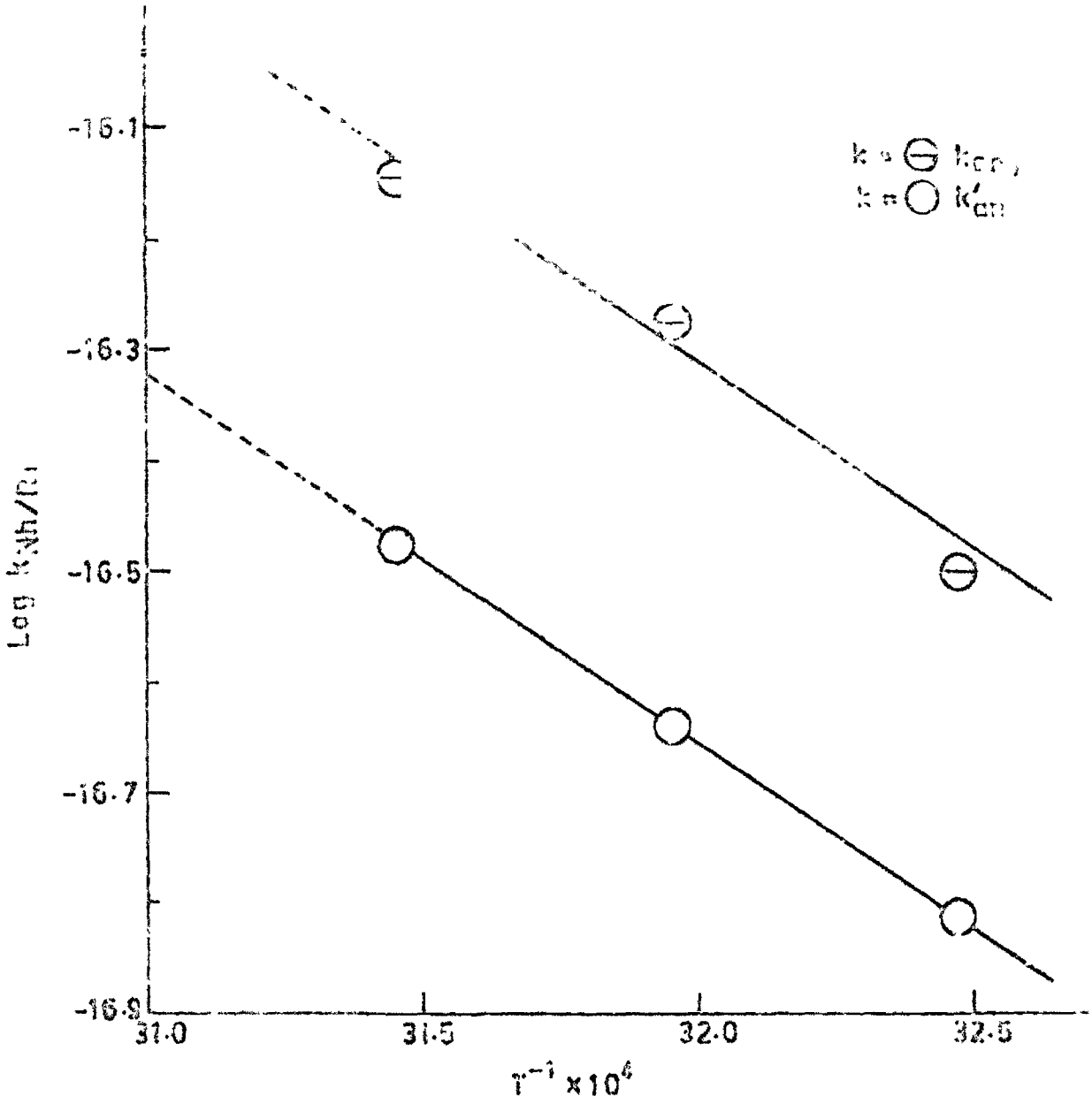


Fig.34 : Arrhenius plots for chromium (III) oxalate with DL-aspartic acid.

TABLE-25 Activation parameters for k_{an}, k'_{an}, K_{IP} and K'_{IP} for the reaction of chromium(III) with DL-aspartic acid.

Rate parameters	ΔH^* (kcal.mole^{-1})	ΔS^* (cal.deg.$^{-1}$mole^{-1})	ΔG^{*a} (kcal.mole^{-1})
k_{an} (sec^{-1})	+15.8	-27.0	+24.4
k^1_{an} (sec^{-1})	+15.5	-27.4	+24.2
k^b_{ex} (sec^{-1})	+26.2	+0.3[c]	-
	ΔH^o (kcal.mole^{-1})	ΔS^o (cal.deg.$^{-1}$mole^{-1})	ΔG^{oa} (kcal.mole^{-1})
K_{IP} (M^{-1})	-6.3	-19.6	-0.1
K'_{IP} (M^{-1})	-6.4	-16.9	-1.0

[a] At 45°C

[b] From D.R. Stranks and T.W. Swaddle, J.Am.Chem.Soc., 93 (1971)2783

[c] Exchange of one ligand only.

plots of ΔG^{*} vs ΔG^{o} (Table 26, Fig. 35) had the slope $\alpha = 0.32$ which confirms an Is mechanism for all the anation reactions described in this thesis.

TABLE-26. Values of ΔG^{o} (free energy for the dissociation of carboxylic group of amino acids) and ΔG^{*} (free energy for the anation of chromium(III)) at 45°C.

Ligand	ΔG^{o} (kcal.mole^{-1})	ΔG^{*} (kcal.mole^{-1})
Glycine	3.4	23.1
DL-α-Alanine	3.4	24.1
DL- Valine	3.1	23.2
DL- Serine	3.1	24.0
DL- Methionine	3.3	23.4
DL-Aspartic acid (zwitterionic)	2.8	23.2
DL- Aspartic acid (monoanionic)	5.6	23.7

Fig.35

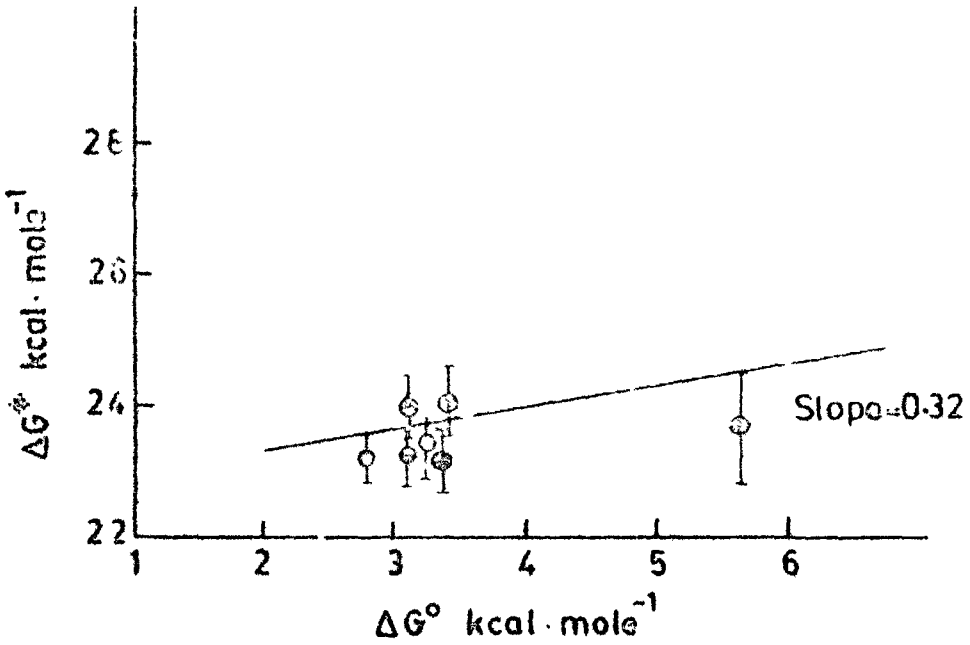


Fig.35: Relation ship between ΔG° and ΔG^{*} for the anation of chromium (III) at 45 C° with glycine —● ; DL - ∝ - alanine – ●; DL - valine – ●; DL – serine – ●; DL–methionine– ●; DL–aspartic acid (zwitterionic)– ●; DL–aspartic acid (monoanionic) – ●.

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APPENDIX

```
// JOB T                                                    CH021   S
// XEQ PRINT
// FOR
*LIST SOURCE PROGRAM
C                                                                    PROGRAM NO.1
C       RATE CONSTANT
C
C       KOBS=CONST-LN(ODE-ODT)
C
*EXTENDED PRECISION
        DIMENSION T(10),ODT(10),X(2,2),Y(2,2),W(2,2),X1(10),X2(10),GX1(10),
       1GX2(10),ODT1(10),AKF(20),AL(80)
        I=1
        ODA=0.065
      1 READ(8,2)NOP,ODE
      2 FORMAT(I5,F10.0)
        READ(8,999)(AL(I),I=1,80)
  999   FORMAT(80A1)
        WRITE(5,999)(AL(I),I=1,80)
        READ(8,3)(ODT(I),I=1,NOP)
        READ(8,3)(T(I),I=1,NOP)
      3 FORMAT(8F10.0)
        D11=0.0
        D12=0.0
        D22=0.0
        DEK1=0.0
        DEK2=0.0
        DO6I=1,NOP
        X1(I)=-ALOG(ODE-ODT(I))
        GX1(I)=X1(I)/2.30258
        D11=D11+1.
        D12=D12+T(I)
        D22=D22+T(I)*T(I)
        DEK1=DEK1+X1(I)
        DEK2=DEK2+X1(I)*T(I)
        AKF(I)=(1./T(I))*ALOG((ODE-ODA)/(ODE-ODT(I)))
      6 CONTINUE
        X(1,1)=D11
        X(1,2)=D12
        X(2,1)=D12
        X(2,2)=D22
        DET=D11*D22-D12*D12
        Y(1,1)=X(2,2)
        Y(1,2)=-X(2,1)
        Y(2,1)=-X(1,2)
        Y(2,2)=X(1,1)
        W(1,1)=Y(1,1)/DET
        W(1,2)=Y(2,1)/DET
        W(2,1)=Y(1,2)/DET
        W(2,2)=Y(2,2)/DET
        A1=W(1,1)*DEK1+W(1,2)*DEK2
        B1=W(2,1)*DEK1+W(2,2)*DEK2
        DIF=0.0
        DO7I=1,NOP
        X2(I)=A1+B1*T(I)
```

```
      GX2(I)=X2(I)/2.30258
      ODT1(I)=ODE-EXP(-X2(I))
      DIL=X1(I)-X2(I)
      DIF=DIF+DIL*DIL
      WRITE(5,8)T(I),ODT(I),X1(I),GX1(I),ODT1(I),X2(I),GX2(I),AK(I)
    8 FORMAT(1X,11F10.6)
    7 CONTINUE
      STA1=SQRT((W(1,1)*DIF)/(D11-2.0))
      STB1=SQRT((W(2,2)*DIF)/(D11-2.0))
      WRITE(5,9)A1,STA1,B1,STB1,DIL,DIF
    9 FORMAT(6E13.5)
      WRITE(5,11)
   11 FORMAT(1X,119('-'))
      I=I+1
      IF(I-100)1,1,10
   10 CALL EXIT
      END
// XEQ
```

```
// J   I                                                    C 102
// E O PRINT
// O
*LIST SOU CE PROGRAM                                                    PROGRAM ...
C       ANATION RATE CONSTANT,ION-PAIR FORMATION CONSTANT
C
C       1/KOBS=A1BF(1/LD)
C
C*XTENDED PRECISION
C       1/KOBS=1/KAN+B1/XX(I)
        DIMENSIONST(15),AK(15),AK(15),SQT(15),X(2,2),XX(2,2),Y(2,2),Y(2,
       1),W(2,2),WW(2,2),AK1(15),AK22(15),DIK1(15),DIK2(15),D1(15),D2(15)
       2,PT(15),ZC1(15),ZC2(15),AX(15),ZZ(15),ZA(15)
        K=1
   30 READ(8,1)NOP,H,DA
    1   FORMAT(I5,2F10.0)
        WRITE(5,65)H
   65   FORMAT(1X,'HYDROGEN ION CONCENTRATION=',E15.6)
        READ(8,2)(ZA(I),I=1,NOP)
        DO201I=1,NOP
2 1     ZZ(I)=1./ZA(I)
        READ(8,2)(AX(I),I=1,NOP)
    2   FORMAT(8F10.0)
        WRITE(5,133)(AX(I),I=1,NOP)
  133   FORMAT(10E11.4)
        ANP=0.0
        DO706I=1,NOP
        AK(I)=ZZ(I)
        PT(I)=AX(I)
        BK(I)=1./ZZ(I)
        ST(I)=1./AX(I)
        SQT(I)=SQRT(1./AX(I))
        ANP=ANP+1.0
  708   CONTINUE
        WRITE(5,101)(BK(I),I=1,NOP)
        WRITE(5,101)(ST(I),I=1,NOP)
  101   FORMAT(1X,10F11.5)
        S1=0.0
        S2=0.0
        S3=0.0
        S4=0.0
        S5=0.0
        S6=0.0
        S7=0.0
        DO10I=1,NOP
        S1=S1+BK(I)
        S2=S2+ST(I)
        S3=S3+BK(I)*ST(I)
        S4=S4+ST(I)**2
        S5=S5+SQT(I)
        S6=S6+SQT(I)**2
        S7=S7+SQT(I)*BK(I)
   10   CONTINUE
        X(1,1)=ANP
        X(1,2)=S2
        X(2,1)=S2
        X(2,2)=S4
        XX(1,1)=ANP
        XX(1,2)=S5
        XX(2,1)=S5
        XX(2,2)=S6
        DET1=ANP*S4-S2*S2
        DET2=ANP*S6-S5*S5
        Y(1,1)=X(2,2)
        Y(1,2)=-X(2,1)
```

```
      Y(2,1)=-X(1,2)
      Y(2,2)=X(1,1)
      YY(1,1)=XX(2,2)
      YY(1,2)=-XX(2,1)
      YY(2,1)=-XX(1,2)
      YY(2,2)=XX(1,1)
      W(1,1)=Y(1,1)/DET1
      W(1,2)=Y(2,1)/DET1
      W(2,1)=Y(1,2)/DET1
      W(2,2)=Y(2,2)/DET1
      WW(1,1)=YY(1,1)/DET2
      WW(1,2)=YY(2,1)/DET2
      WW(2,1)=YY(1,2)/DET2
      WW(2,2)=YY(2,2)/DET2
      AK1=W(1,1)*S1+W(1,2)*S3
      B1=W(2,1)*S1+W(2,2)*S3
      AK2=WW(1,1)*S1+WW(1,2)*S7
      B2=WW(2,1)*S1+WW(2,2)*S7
      CK1=AK1
      CK2=AK2
      DIF1=0.0
      DIF2=0.0
      DSF1=0.0
      DSF2=0.0
      F1=0.0
      F2=0.0
      DO119I=1,NCP
      ZC1(I)=AK1+B1*ST(I)
      ZC2(I)=AK2+B2*SQT(I)
      AK11(I)=1./ZC1(I)
      AK22(I)=1./ZC2(I)
  119 CONTINUE
      DO11I=1,NOP
      DEL1=BK(I)-ZC1(I)
      DEL2=BK(I)-ZC2(I)
      DIK1(I)=((AK(I)-AK11(I))/AK(I))*100.
      DIK2(I)=((AK(I)-AK22(I))/AK(I))*100.
      D1(I)=AK(I)-AK11(I)
      D2(I)=AK(I)-AK22(I)
      F1=F1+D1(I)
      F2=F2+D2(I)
      DSF1=DSF1+(AK(I)-AK11(I))**2
      DSF2=DSF2+(AK(I)-AK22(I))**2
      DIF1=DIF1+DEL1*DEL1
      DIF2=DIF2+DEL2*DEL2
   11 CONTINUE
      AF1=F1/ANP
      AF2=F2/ANP
      Q1=0.0
      Q2=0.0
      DO71I=1,NOP
      Q1=Q1+(D1(I)-AF1)**2
      Q2=Q2+(D2(I)-AF2)**2
   71 CONTINUE
      WRITE(5,99)(AK(I),I=1,NOP)
   99 FORMAT(11E11.5)
      WRITE(5,32)(AK11(I),I=1,NOP)
      WRITE(5,32)(AK22(I),I=1,NOP)
      WRITE(5,32)(DIK1(I),I=1,NOP)
      WRITE(5,32)(DIK2(I),I=1,NOP)
   32 FORMAT(1HO,1X,10E11.5)
      STAK1=SQRT((W(1,1)*DIF1)/(ANP-2.0))
```

```
      STCK1=EXP(STAK1)
      STB1=SQRT((W(2,2)*DIF1)/(ANP-2.0))
      STAK2=SQRT((W(1,1)*DIF2)/(ANP-2.0))
      STCK2=EXP(STAK2)
      STB2=SQRT((W(2,2)*DIF2)/(ANP-2.0))
      SQZ1=SQRT(DSF1/(ANP-1.0))
      SQZ2=SQRT(DSF2/(ANP-1.0))
      SQD1=SQRT(Q1/(ANP-1.0))
      SQD2=SQRT(Q2/(ANP-1.0))
      XK1=1./AK1
      XK2=(AK1/B1)*(H+DA)/DA
      XK3=(1./B1)*(H+DA)/DA
      XK4=AK1/B1
      STX1=(STAK1/AK1)*XK1          STX2=(STB1/B1)*XK2
      STX3=(STB1/B1)*XK3
       STX4=(STB1/B1)*XK4
      STDA=SQRT(DA*SQZ1/(NOP-1))
      WRITE(5,12)AK1,STAK1,B1,STB1,AK2,STAK2,B2,STB2,DIF1,DIF2
   12 FORMAT(1HO,2X,10E11.4)
      WRITE(5,38)XK1,STX1,XK2,STX2,XK3,STX3,DA,STDA,XK4,STX4
   38  FORMAT(1X,10E11.4)
      WRITE(5,13)CK1,STCK1,CK2,STCK2,SQZ1,SQZ2,DSF1,DSF2
   13 FORMAT(/1X,8E14.6)
      WRITE(5,72)AF1,SQD1,AF2,SQD2,Q1,Q2
   72 FORMAT(1HO,2X,6E13.6/)
      WRITE(5,14)
   14 FORMAT(1X,119('-'))
      K=K+1
      IF(K-60)30,30,31
   31 CALL EXIT
      END
// XEQ
```